X-RAY PEAK AREA AS A METHOD OF CHARACTERIZING PETROLEUM COKES

V. Dean Allred

Marathon Oil Company
Denver Research Center
P. O. Box 269
Denver, Colorado 80120

OVERVIEW

X-ray diffraction analysis is a versatile tool in the characterization of petroleum coke. In 1963 personnel at Marathon's Research Center worked out a procedure where X-ray diffraction analysis of a coke sample could be used to classify it broadly with respect to the linear CTE (Coefficient of Thermal Expansion) value of graphite which would be produced by it.[1] This technique was based on the observation that a plot of the CTE versus the logarithm of the ratio of peak height to width at one-half height gave a reasonably straight line function. Calibration was by comparison to a series of standard samples.

Success of the procedure depended on firing a sample to the same conditions of time and temperature. Initially, samples of the standards were fired simultaneously with the unknown and excellent results were obtained. However, as the supply of standard cokes was depleted, it was evident that some other procedure was needed. Therefore, a series of standard fired samples were prepared. These standards were then to be used over and over again as calibration standards. The critical operations then became the technique for preparing the unknown samples and the mounting of individual samples in the holder of the X-ray diffraction unit. The most sensitive item was the calcining procedure since both the peak height and width were strongly dependent on the firing history (temperature and time at temperature). That is, over the calcining temperature range, as the firing temperature was increased the peak height (intensity) increases exponentially, and the peak width to a lesser degree decreases in a similar manner.

At an early date it was recognized that for almost all delayed petroleum cokes, the average peak width was almost a unique function of the firing history and not much affected by the coke type. Whereas, the peak height was extremely sensitive to the coke type for comparable firing conditions. The average peak width, therefore, could be used as an indicator of the correct firing history. Comparing the peak width for the unknown with that of the standard samples indicated whether the X-ray data was suitable for a CTE correlation.

Experience soon showed that it was difficult to adequately reproduce firing conditions. This problem led to a re-evaluation of the X-ray peak width and height relationships to determine if correction factors could be applied to bring the data in line or whether some other relationship could be found. As a result, it was discovered that the peak height times the average peak width (in consistent X-ray units) was remarkably constant over a fairly broad temperature range ($\sim$ 2400 to 2600°F). Whereas, the ratio of peak height over width was actually changing exponentially (Figure 1). Fortunately, this constant area region also coincided with the temperature range where petroleum cokes are usually calcined. Therefore, the extreme care used in firing of cokes for X-ray/CTE correlation is now unnecessary, the accuracy of the correlation has improved, and it is possible to evaluate cokes calcined by others, e.g., in commercial calciners.

EXPERIMENTAL

Sample Preparation

Assuming that the firing of the coke sample has been within the required temperature limits, the most critical item of sample preparation becomes the operator's technique in packing or loading the sample holder. However, sample preparation consistent with good X-ray diffraction analysis must also be practiced, i.e., obtaining a representative sample and reduction to X-ray sample size.

Loading of the sample in the holder is critical since some preferred orientation can be given to the coke -- particularly for low CTE cokes, which will influence the intensity of the diffraction peak. Good reproducible results, therefore, depend on the experience and care used by the operator in loading and operating his equipment so that it is done the same way each time. (In our laboratory, samples used as calibration standards are reloaded each time as part of the procedure.) If the calibration data are essentially constant for successive determinations, one can be relatively sure that the data from the unknown will also be consistent. It is also good practice for the spectroscopist to run a minimum number of determinations (usually two or three) for the sample and the standards to see that the data are self consistent.

Data Evaluation

The only X-ray diffraction peak that has proven valuable for characterizing delayed petroleum cokes fired in a temperature range up to 3000°F is the 002 graphite line. A typical trace showing this peak is given as Figure 2. In obtaining the required data, the peak height (H) and width at half-height ($\beta_{1/2}$) are taken from the chart in terms of linear measurement, however, it should be noted that they do not represent consistent units. That is, the peak width is caused by scattering and is a function of the size of the diffracting crystallites. It has the units of angular scan (2θ) in degrees, as determined by the geometry of the goniometer being used. Peak height on the other hand is a measure of the intensity of the diffracted X-ray radiation. Normally, it is measured by a radiation counter and has the dimensions of so many counts per unit of time.

In making an X-ray evaluation of petroleum coke for correlation purposes, it is therefore necessary to use fixed operating conditions. Further, it is questionable whether data from one X-ray unit should ever be compared directly with that of another. On the other hand, through the use of the calibration standards, differences between two different X-ray units can be readily resolved, and data correlated accordingly.

Finally, it is also recognized that the peak width has in it a factor caused by inherent scattering due to the instrument itself. This is usually quite small and remains constant if the alignment of the X-ray unit does not change. In calculating crystallite size it is important to correct for the machine scattering factor (β_0). However, in making these correlations, the experimental width has been used directly since a change in β_0 would be indicated by a change in the value determined for the calibration standard.

DISCUSSION

Temperature Effects

Firing temperatures in excess of 2000°F are desirable for the X-ray/CTE correlations. The temperature sensitivity of the peak height and width for a typical petroleum coke is shown in Figure 3. As indicated in this figure, some anomalies exist in the X-ray data for coke fired at temperatures below 1800°F. The anomalous behavior is particularly noticeable in the average peak width in that it at first increases and then reverses itself and decreases with temperature. The peak height on the other hand remains almost constant through this particular temperature range. The low temperature anomaly in peak width is probably indicative of a structural change as the carbonaceous polymer (green coke) decomposes to form carbon. (The helium density also undergoes an anomalous change in the temperature range 1400 to 1600°F.)

Time Effects

The firing history of calcined petroleum coke depends on temperature and time at temperature. The peak width function most nearly reflects the firing history. The temperature has a greater effect than time, nevertheless, time at temperature can be an important variable particularly when short-time periods are involved.

Figures 4a and 4b show the change in 002 peak width and height, respectively, as a function of time for samples of a typical petroleum coke heated at a constant temperature for various periods of time. For convenience, these data are plotted with the reciprocal of time as a coordinate since the change in the width function decreases rapidly with time and approaches a limiting value at infinite time. The coke used in these determinations had been previously devolatilized at 1800°F ($\beta_{1/2} \sim 3.00$) to stabilize them. In obtaining the data, the coke samples (in graphite crucibles) were placed in a preheated oven and allowed to come up to temperature (about 30 minutes) before timing commenced. At predetermined times individual crucibles were withdrawn and cooled under a carbon dioxide atmosphere.

Figure 4c shows the relationship between peak area and the calcining time. These data show -- even with appreciable scatter of data points -- that the peak area is independent of time-temperature relationship over a considerable range (2400 to 2600°F over times from 5 minutes to 24 hours).

Relationship of Coke Type

Figure 5 is a plot of the average peak width versus peak area obtained for coke samples produced from vacuum residuum, topped crude oil, and thermal tars. (CTE range from 4 to 30 [x 10^{-7}]). As previously noted, the width is relatively independent of the delayed coke type (i.e., high or low CTE). On the other hand, the height -- and subsequently the area -- is strongly affected by the coke type. Nevertheless, the product of the width by the height ($H\beta_{1/2}$) remains characteristically constant for a given coke type over the same range of peak width ($\beta_{1/2} \sim 1.25$ to 1.75).

The X-ray/CTE Correlation

Figure 6 shows a plot of the X-ray peak area versus the CTE factor obtained for graphite produced from it for coke used as calibration samples. Experience gained during the past several years has shown that most delayed petroleum cokes will produce graphite with a CTE value comparable to its relative position on such a calibration curve.

SUMMARY

A technique to determine an X-ray/CTE correlation factor for calcined petroleum coke has been developed. This procedure permits classification of a petroleum coke as to its potential use and value without having to prepare a graphite test specimen.

REFERENCE

1. Stout, C. F., Janes, M., and Biehl, J. A., "Research and Development on Advanced Graphite Materials", p. 20-23, XXXVI Technical Documentary Report WADD TR 61-72, August, 1964, U.S.A.F. Systems Command, Wright-Patterson Air Force Base, Ohio.

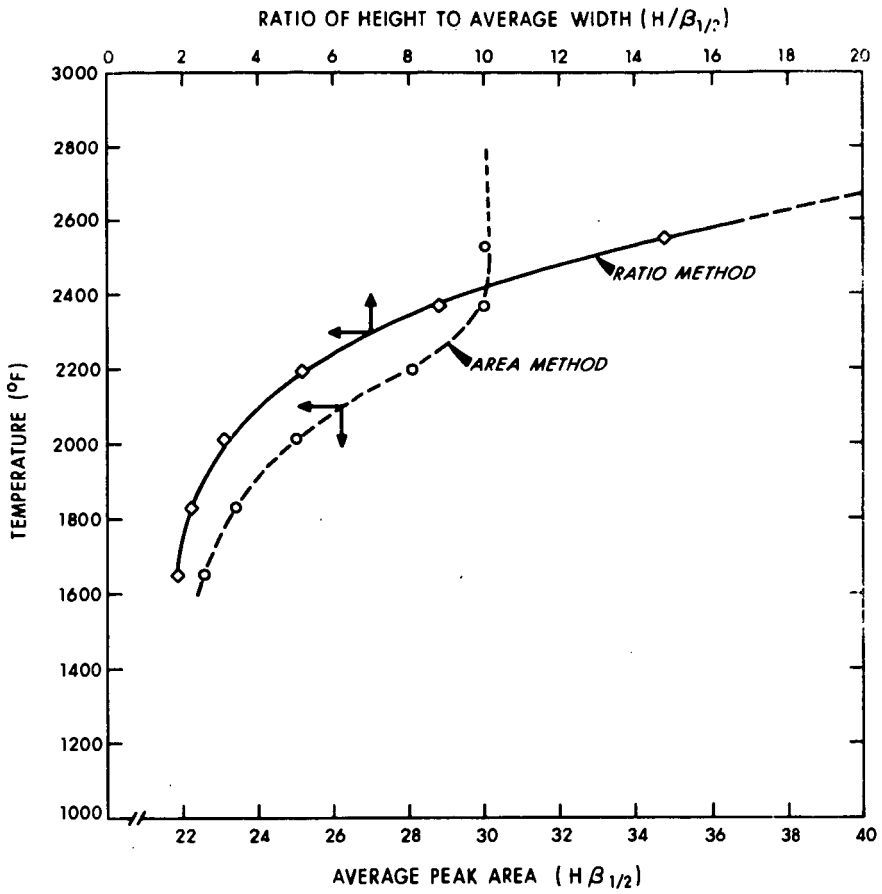RATIO OF HEIGHT TO AVERAGE WIDTH ($H/\beta_{1/2}$)

FIGURE 1. DATA SHOWING THE TEMPERATURE SENSITIVITY OF THE 002 X-RAY
PEAK HEIGHT VS WIDTH AT ONE-HALF HEIGHT AS A RATIO AND AN AREA.
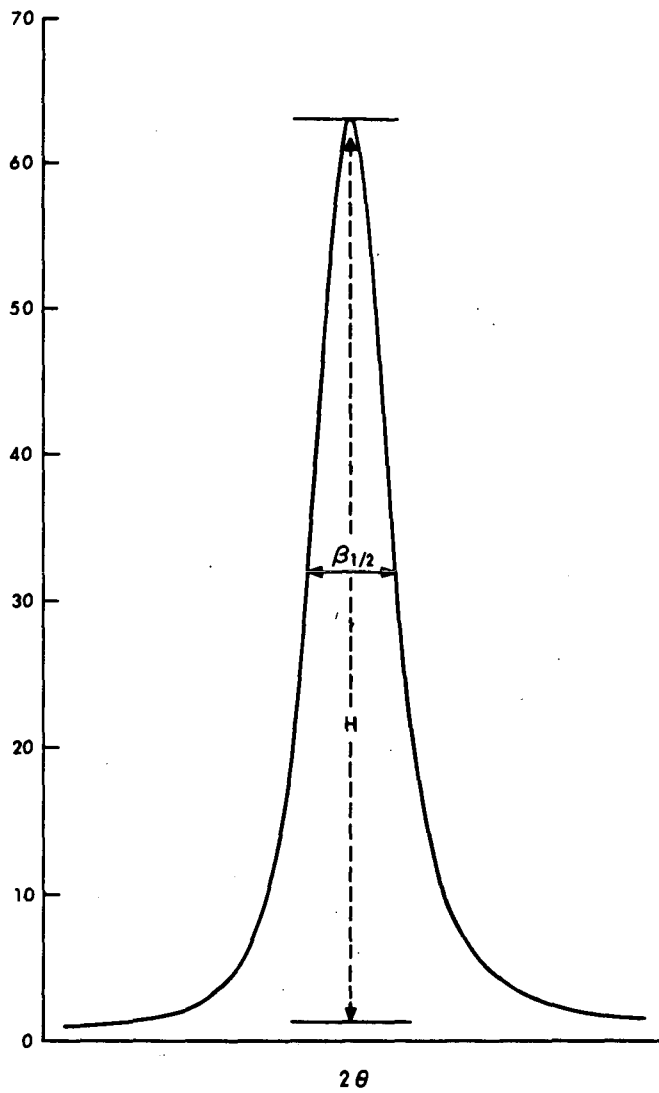
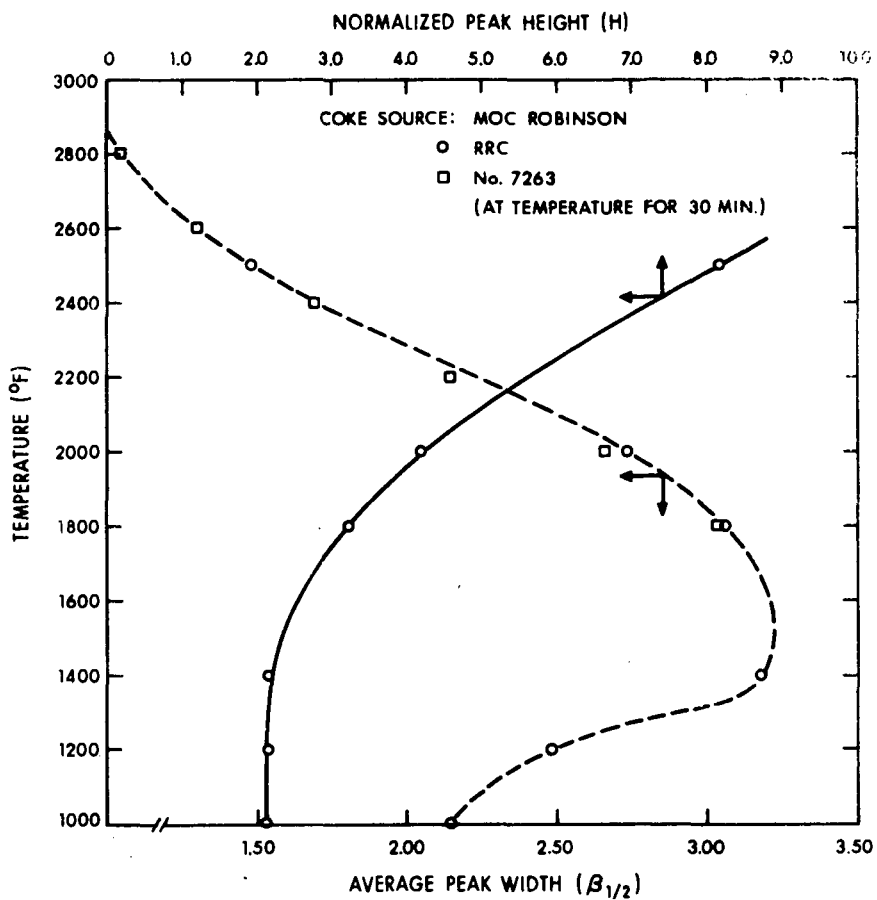FIGURE 2. TYPICAL CHART TRACE SHOWING THE 002 DIFFRACTION LINE.

FIGURE 3. TEMPERATURE SENSITIVITY OF AVERAGE PEAK WIDTH ($\beta_{1/2}$) AND PEAK HEIGHT (H).
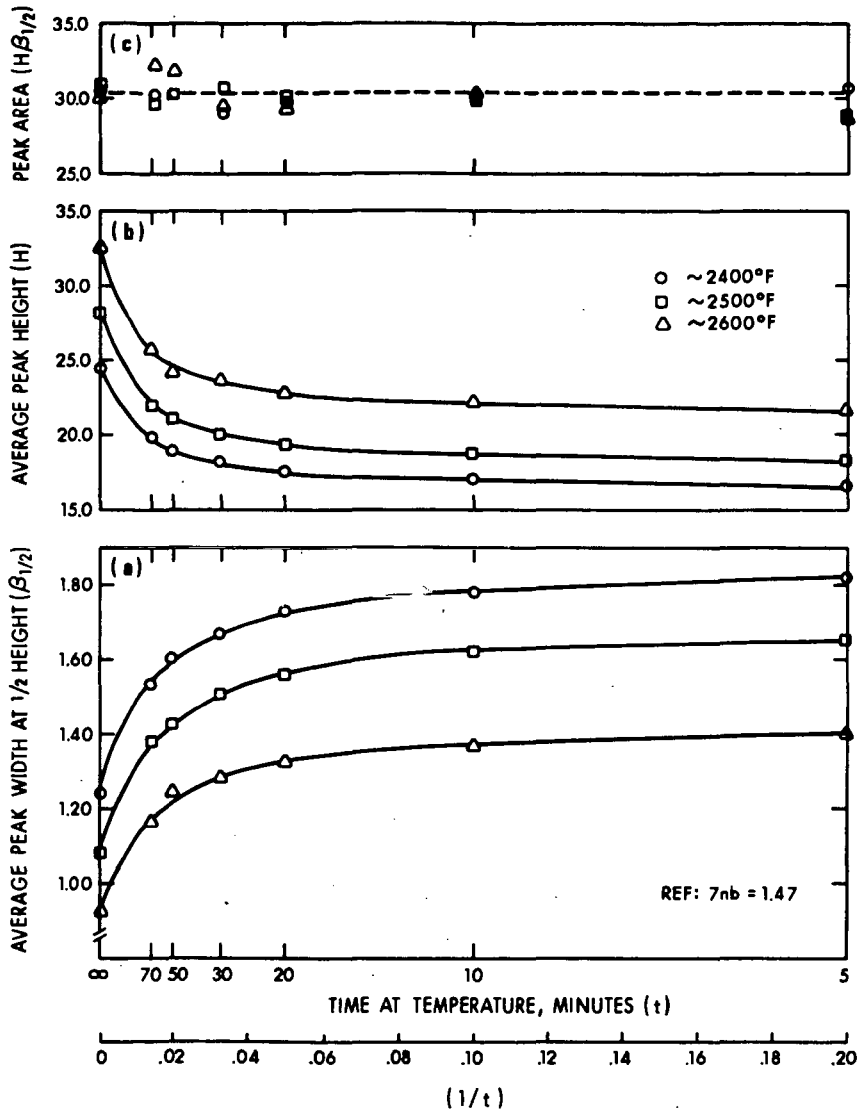
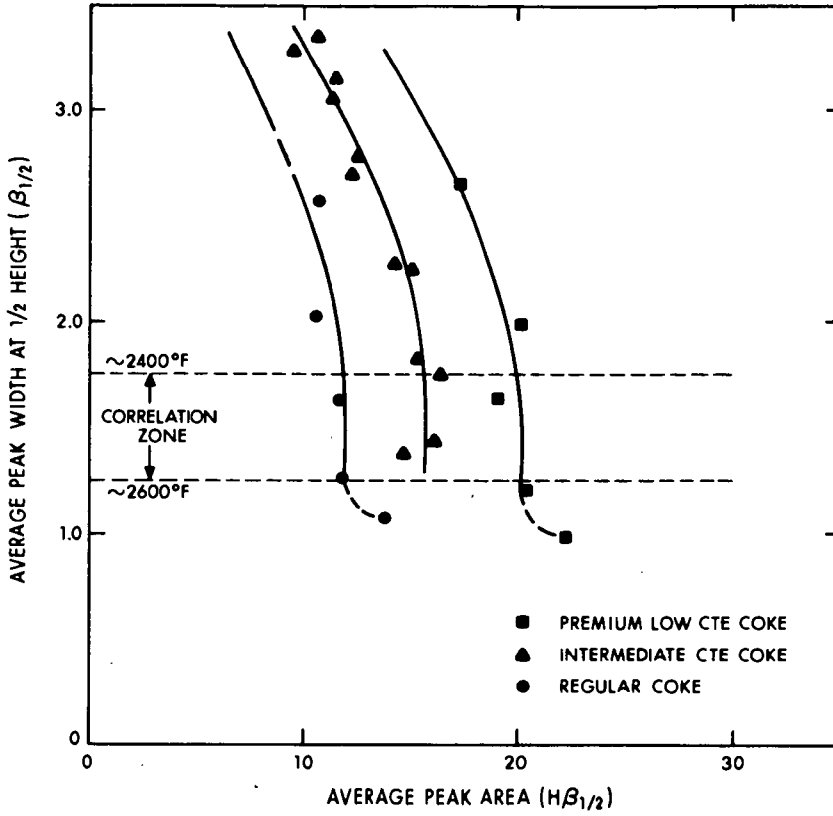FIGURE 4. a-c. TIME-TEMPERATURE EFFECTS WITH AVERAGE PEAK WIDTH, PEAK HEIGHT, AND AREA.

FIGURE 5. RELATIONSHIP BETWEEN COKE TYPE AND AREA AS A FUNCTION OF AVERAGE PEAK WIDTH.
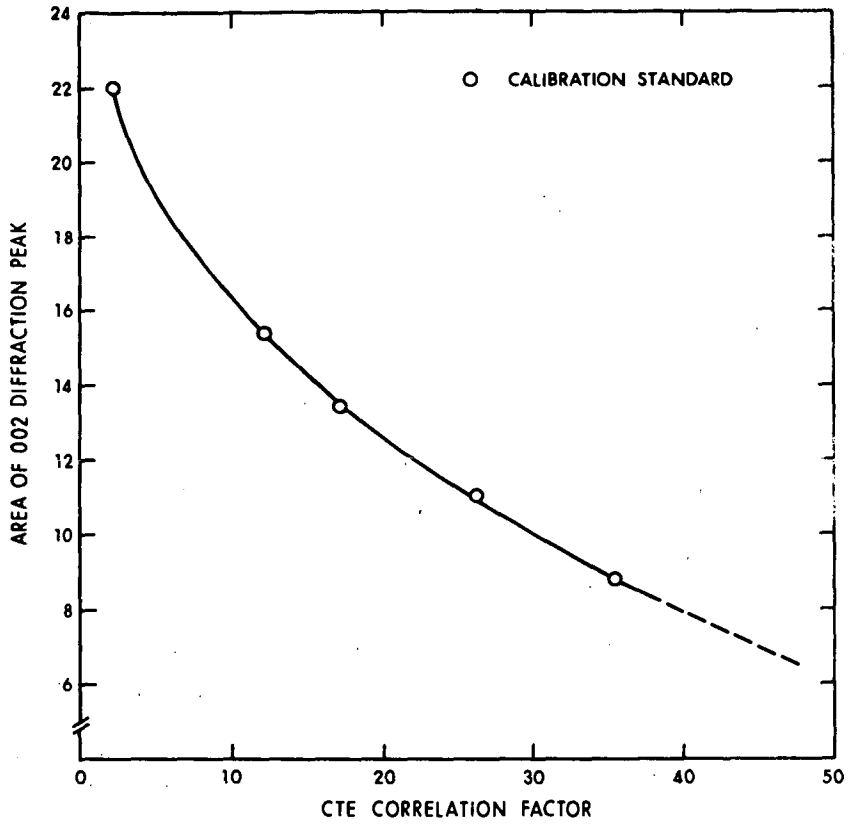
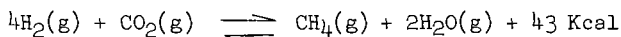FIGURE 6. TYPICAL CTE/X-RAY CORRELATION CALIBRATION CURVE.

KINETICS OF CARBON DIOXIDE METHANATION ON
A RUTHENIUM CATALYST

Peter J. Lunde and Frank L. Kester

Hamilton Standard Division,
United Aircraft Corporation
Windsor Locks, Connecticut, 06096

INTRODUCTION

The catalytic hydrogenation of carbon dioxide to methane

$$4H_2(g) + CO_2(g) \rightleftharpoons CH_4(g) + 2H_2O(g) + 43 \text{ Kcal}$$

is often called the Sabatier reaction, after the Belgian chemist who investigated the hydrogenation of hydrocarbons using a nickel catalyst. The Sabatier reaction is becoming of commercial interest for the manufacture of natural gas from the products of coal gasification. The reverse reaction, of course, is called steam reformation and is a commercial method for hydrogen manufacture.

This paper developed from work performed under contract to NASA to investigate the Sabatier reaction as a step in reclaiming oxygen within closed cycle life support systems. Carbon dioxide from the cabin atmosphere is thus changed into water vapor which is electrolyzed to provide oxygen for the cabin plus one-half the hydrogen required for the Sabatier reaction. The rest of the hydrogen is provided from the electrolysis of stored water, which produces breathing oxygen as a by-product, reducing the proportion of available carbon dioxide which must be reacted and assuring excess carbon dioxide in the feed mixture.

The Sabatier reaction is a reversible, highly exothermic reaction which proceeds at a useful rate at the low temperatures required for high yields only when a catalyst is used. Dew, White, and Sliepcevitch (1) studied this reaction using a nickel catalyst. This paper examines the kinetics of the reaction using a Ruthenium catalyst, and derives from experimental data a correlation describing the kinetics of this catalysis in the $400^{\circ}F$ to $700^{\circ}F$ temperature range.

Thermodynamics

Equilibrium compositions for hydrogen and carbon dioxide mixtures at 1 atm are shown in Figure 1, which was prepared with the aid of a computer program developed by United Aircraft Research Laboratories using free energies from Wagman (2). Carbon and carbon monoxide are possible products, as well as methane and water vapor. The reaction proceeds as written

$$4H_2(g) + CO_2(g) \rightleftharpoons 2H_2O(g) + CH_4(g)$$
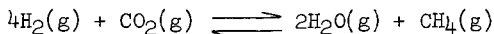
for molar feed ratios ($H_2:CO_2$) of over 3.5:1 at temperatures from $400^{\circ}F$ to $700^{\circ}F$.

Low temperatures favor high conversions. At $700^{\circ}F$ and a feed ratio ($H_2:CO_2$) of 3.5:1 the equilibrium conversion of H_2 is only 90%, while at $400^{\circ}F$ it is about 99%.

As the feed ratio falls below 3.5:1, carbon becomes thermodynamically stable at higher and higher temperatures. At 3:1, carbon deposition is possible only below $500^{\circ}F$ while at 2:1 it is stable below $1100^{\circ}F$.

Carbon monoxide formation is thermodynamically possible above $700^{\circ}F$, where the reaction encounters the well-known "water gas shift".

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$
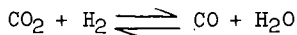
This does not cause a limitation in maximum operating temperature because any carbon monoxide formed is converted to other products downstream in the reactor's subsequent $400^{\circ}F$ - $700^{\circ}F$ temperature zone which is necessary for a practical yield.

<div align="center">EXPERIMENTAL</div>

Catalyst Selection

Thompson (3) conducted a Sabatier catalyst screening program for the US Air Force. Four catalysts were experimentally evaluated:

1) Nickel (80% Ni and NiO) on kieselguhr)
2) 0.5% ruthenium (on alumina)
3) 0.5% rhodium (on alumina)
4) 0.5% cobalt (on alumina)

Ruthenium and nickel were found to be appreciably more active catalysts for promoting the Sabatier reaction. Nickel, however, presented several operating problems.

1) Slow deterioration over the test period, attributed to sulfur poisoning.
2) Reactor startup in hydrogen was advisable to assure reduction of nickel to its most active form.
3) Carbon deposition was reported at $650^{\circ}F$ to $700^{\circ}F$.

Ruthenium had none of these problems, and was somewhat more active than the nickel as a catalyst. Furthermore, there was a potential for even more activity if heavier loadings of the metal on the substrate are used.

Consequently a 0.5% ruthenium catalyst on 1/8 in x 1/8 cylindrical alumina pellets was selected for further investigation. The prepared catalyst, Englehard type "E", was purchased from

Englehard Industries Division
Englehard Minerals and Chemicals Corp.
113 Aster Street
Newark, N. J.

The manufacturer furnished no lot number or other specific information but did disclose that the catalyst performed within the limits of their internal specifications. Superficial examination of the pellets indicated the ruthenium did not penetrate more than 1/2 mm into the alumina indicating that pore diffusion was not likely to be important in the performance of this catalyst. The bulk density of the pellets was measured as 1.0 g/cc.

Approach

The ruthenium catalyst is relatively new and there are no published quantitative data from which the kinetics can be determined. Consequently, an experimental apparatus was designed and a program to acquire rate data was begun.

Hydrogen and carbon dioxide were fed continuously to the experimental apparatus. The test reactor, a tube filled with catalyst and held isothermal by immersion in a molten salt bath, was made small so that the conversion of unreacted feed was low but measurable at the lowest operating temperature, minimumizing the reaction heat released. At higher temperatures part of the feed was passed through a large "supply" reactor providing a partly reacted feed to the test reactor which reduced the reaction rate and the reaction heat released.

Steady state conversions were determined from flow information and chromatographic analyses of the test reactor inlet and outlet streams. Mass flow to the reactor was held steady for runs at several temperatures, giving data for calculation of the reaction activation energy, which describes the temperature dependence of the reaction rate. Additional runs were made at constant temperature to determine the basic reaction rate constant.

Feed flow ratios ($H_2:CO_2$) of 2:1 and nearly 4:1 were investigated. Temperatures of $400°F$ to $700°F$ were selected for activation energy data accumulation since at temperatures over $700°F$ the reaction proceeds rapidly and is complicated by carbon dioxide formation, while $400°F$ is low enough to allow virtually complete conversion of the feed in a practical reactor.

Apparatus

A schematic for the complete experimental rate data apparatus is shown in Figure 2.

The feed rates of hydrogen and carbon dioxide were set externally using laminar flowmeters. Electronic differential pressure sensors converted a differential pressure flow signal to an electrical voltage which was read on a digital voltmeter. The flowmeter calibrations are shown in Figure 3.

When desired, partially reacted feed was produced by passing part of the mixed feed flow through a "supply" Sabatier reactor. This reactor, which also used a ruthenium catalyst, was heated to about $650°F$ and was large enough to react 80% - 90% of the stoichiometrically lean feed constituent.

Sampling

All samples except the inlet feed were fed to a Bendix process chromatograph at very low flow (Figure 2, S1, S2, S4, S5). The inlet feed sample (S3) was taken by actuating two three-way valves which directed the entire feed stream through the chromatograph sampling valve. A sample could be taken in this manner without changing the feed flow rate. When other samples were being taken the pressure drop of the chromatograph sampling valve (about 0.6 - 0.8 psi) was simulated in the feed line with a precision metering valve (marked "ADJ") set to maintain a constant pressure at PI-2 so that there was no transient when the feed sample valves were actuated. Heating tape and heated valve boxes were necessary throughout the sampling system to prevent water from condensing in the sample lines.

The process gas chromatograph analyzed feed and effluent gases using samples of equal volume for analysis. Peaks were automatically gated, attenuated and

recorded. Peak heights were then manually measured and logged as raw composition data. Components analyzed were H_2O, CO_2, H_2, CO, CH_4, N_2, Ar, and O_2, but the last three were not present in significant quantities. A typical chromatogram is shown in Figure 4. Each analysis took 13 minutes and was always repeated before data was recorded.

The chromatograph was calibrated by using pure CO_2, H_2, and CH_4, at several pressures in the 0-1 atm range. The chromatographic peak heights then corresponded to partial pressures of the calibrated constituents. Water was calibrated indirectly using Sabatier reactor effluent, in which the partial pressure of water vapor was necessarily exactly twice that of the methane which was already calibrated. Final calibration curves for the chromatograph are shown in Figure 5.

After the chromatograph was calibrated, the hydrogen peak signal became erratic during the data collection phase. Successful gas analyses were continued by taking the correct hydrogen partial pressure as equal to the difference between analysis pressure and the sum of the other constituents as determined from their peak heights and calibration curves. The accuracy of this method was confirmed later in this work after the electronic malfunction responsible was repaired.

Test Reactor

The differential reactor used for the actual kinetic study was made from 1/2 in. stainless steel tubing (0.43 in ID x 1.75 in). The catalyst charge of 3.58 grams (about eighty 1/8 in. x 1/8 in. cylindrical alumina pellets coated with 1/2% ruthenium) filled the 4.15 cc reactor tube. The reactor was called the "differential" reactor because its purpose was to convert only a small portion of the feed stream to the Sabatier products.

The differential reactor assembly, consisting of a feed preheating coil, thermocouples and sample tubes (Figure 6) was submerged in an oven-heated molten salt bath to keep the reactor isothermal, because of the high heat of reaction. Thermocouples were installed in the inlet stream (T2), outlet stream (T4), at the center of the reactor (T3), and on the reactor wall (T5). Samples could be taken from the feed (after preheat) (S4), effluent (S5), and (externally) from the feed before entering the reactor.

At the low end of the temperature range ($400°$ - $500°F$) reaction rates were low and the reactor wall and center thermocouples agreed $\pm 1°F$. At higher temperatures the reaction rate was high and the reaction rate was reduced so that the temperature differential was held below $10°F$ by partly reacting the inlet feed before it entered the differential reactor. Using this technique good experimental data could be taken from $400°F$ to $700°F$ in a single reactor with a constant feed rate.

DISCUSSION

Since the mechanism for ruthenium catalysis is unknown, gas phase type kinetics are proposed for the reaction:

$$4H_2(g) + CO_2(g) \underset{kr}{\overset{kf}{\rightleftharpoons}} 2H_2O(g) + CH_4(g)$$
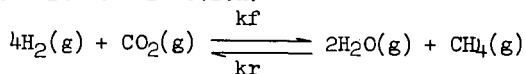
where k_f and k_r represent reaction rate constants for the forward and reverse reactions, respectively. Thus

$$- \frac{d\left[P_{CO_2}\right]}{dt} = k_r^n \left[P_{H_2O}\right]^{2n} \left[P_{CH_4}\right]^n - k_f^n \left[P_{CO_2}\right]^n \left[P_{H_2}\right]^{4n} \qquad (1)$$

where n is an emperical constant equal to 1 for pure gas phase kinetics.

When equilibrium is achieved, $-d\left|P_{CO_2}\right|/\ dt = 0$, and equation (1) becomes

$$K_e = \frac{k_f}{k_r} = \frac{\left[P_{H_2O}\right]^2\left[P_{CH_4}\right]}{\left[P_{CO_2}\right]\left[P_{H_2}\right]^4} \tag{2}$$

and the emperical exponent applied to the exponential coefficients cancels so that the equilibrium constant, K_e, is defined as a classical thermodynamics.

Noting the $K_e^n = k_f^n/k_r^n$, if equation (1) is rewritten $\tag{3}$

$$-\frac{d\left[P_{CO_2}\right]}{dt} = k_f^n \left\{ \left[P_{CO_2}\right]^n\left[P_{H_2}\right]^{4n} - \frac{\left[P_{CH_4}\right]^n\left[P_{H_2O}\right]^{2n}}{(Keq(T))^n} \right\} \tag{4}$$

then the temperature dependence of the reaction rate constants can be described by the general Arrhenius relationship

$$k_f^n(T) = k\ \exp(-E_a/RT) \tag{5}$$

and thus the final form of the rate expression is

$$-\frac{d\left[P_{CO_2}\right]}{dt} = k\ \exp\ (-E_a/RT) \left\{ \left[P_{CO_2}\right]^n\left[P_{H_2}\right]^{4n} - \frac{\left[P_{CH_4}\right]^n\left[P_{H_2O}\right]^{2n}}{(Keq(T))^n} \right\} \tag{6}$$

where k (the rate constant) and Ea (the activation energy) and n (catalyst coefficient) are constants to be determined for the experimental data.

To find the activation energy E_a and catalyst coefficient n for equation (6) the logarithms of both sides are taken. Rearrangement then gives

$$Y \equiv \ln \frac{-d\left[P_{CO_2}\right]/dt}{\left[P_{CO_2}\right]^n\left[P_{H_2}\right]^{4n} - \frac{1}{K_{eq}^n}\left[P_{CH_4}\right]^n\left[P_{H_2O}\right]^{2n}} = \left[\frac{E_a}{R}\right]\left[\frac{1}{T}\right] + \ln k \tag{7}$$

which is of the form $Y = mX + b$. A plot of Y vs $1/T$ thus has a slope of Ea/R, enabling determination of Ea. The catalyst coefficient n can be determined by trial because improper values of n do not give a linear plot of experimental data.

With Ea and n determined, equation (6) can be now integrated to obtain a value of rate constant k for each experimental run.

Rearranging and solving equation (6) for k

$$k = e^{-E_a/RT} \left[\frac{dP_{CO_2}}{dt}\right] \left[\frac{-1}{\left[P_{CO_2}\right]^n\left[P_{H_2}\right]^{4n} - \frac{1}{K_{eq}^n}\left[P_{CH_4}\right]^n\left[P_{H_2O}\right]^{2n}}\right] . \tag{8}$$

If the change in P_{CO_2} as it passes through the reactor is defined as X, then the variables can be separated

$$k = e^{-Ea/RT} \frac{dX}{dt} \left[\frac{-1}{\left[P_{CO_2}^{in} - X\right]^n \left[P_{H_2}^{in} - 4X\right]^{4n} - \frac{1}{K_{eq}^n} \left[X\right]^n \left[2X\right]^{2n}} \right] \quad (9)$$

where $P_{CO_2}^{in}$ and $P_{H_2}^{in}$ are inlet partial pressures.

Integrating equation (9) from reactor inlet to outlet,

$$k = e^{-Ea/RT} \frac{\displaystyle\int_{o}^{P_{CO_2}^{in} - P_{CO_2}^{out}} \frac{dX}{\left[P_{CO_2}^{in} - X\right]^n \left[P_{H_2}^{in} - 4X\right]^{4n} - \frac{1}{K_{eq}^n}\left[X\right]^n\left[2X\right]^{2n}}}{\displaystyle\int_{t_{in}}^{t_{out}} dt} \quad (10)$$

Since space velocity $S_v = \frac{1}{t}$ where t is contact time,

$$k = e^{-Ea/RT} S_v \int_{o}^{P_{CO_2}^{in} - P_{CO_2}^{out}} \left[\frac{dX}{\left[P_{CO_2}^{in} - X\right]^n \left[P_{H_2}^{in} - 4X\right]^{4n} - \frac{1}{K_{eq}^n}\left[X\right]^n\left[2X\right]^{2n}} \right] \quad (11)$$

The integral involves only inlet and outlet concentrations, known kinetic constants and the running variable X, and can be solved by numerical or graphical techniques. Values of $K_{eq}(T)$ were obtained from (2).

A standard fourth order Runge-Kutta numerical integration technique was carried out for each test run using a computer program written explicitly for this work. The Runge-Kutta method, which employs a Taylor series expansion of the derivative function, was selected because of its accuracy and stability (4).

RESULTS

Two series of data were taken using the differential test reactor. The activation energy series was run over a wide temperature range at low reaction rates to determine activation energy and catalyst coefficient. The reaction rate series was run at a single temperature and varying reaction rates to determine the reaction rate coefficient.

Table I shows the complete experimental data after preliminary processing.[1] Table II shows the results of activation energy calculations from equation (7) using selected runs. Table III shows the results of integration of other selected runs to calculate a rate constant according to equation (11). Table IV indicates the criteria for selecting runs for these calculations.

The <u>activation energy</u> series was started at 400°F and the temperature gradually raised to 700°F while the conversion of the inlet gas was raised from 0% to 96% to keep the composition change across the differential reactor small (Runs 519-551). Volumetric flow of the feed gas was held steady except for two lower value runs at the start. The ratio of $H_2:CO_2$ in the feed gas was held just below stoichiometric (at 3.8) for the first temperature sweep (Runs 519-534), and at about 2.0 for the second (Runs 538.50 - 551).

The <u>reaction rate</u> series was run at bath temperatures of 580°F and 520°F and at inlet flow ratios of 1.9 and 2.9, respectively (Runs 560-581). Inlet conversions were varied from 0% to 84%. Two final runs were taken at flow ratios just over stoichiometric (at 4.1) using lower bath temperatures providing unreacted feed gas at 435°F and 475°F (Runs 590 and 591).

The lower inlet flow ratios of $H_2:CO_2$ in each series was within the range for which carbon deposition was thermodynamically stable (Figure 1). No evidence for such deposition was observed in these tests in performance degradation or after post-test catalyst examination.

<div align="center">EXPERIMENTAL DATA REDUCTION</div>

A data reduction computer program was used to produce the data presented in Table I.

<u>Inlet and Outlet Partial Pressures</u> - Inlet analysis total pressure was taken as the arithmetic average between supply reactor pressure (PI-2, Figure 2) and differential reactor inlet pressure (PI-3). CO_2, H_2O, and CH_4 partial pressures were determined from chromatographic peak heights and H_2 taken as the remaining constituent by difference, as discussed in "Sampling", above. The partial pressures were then normalized to total 1.000, thus becoming mol fractions, and then mutiplied by the inlet reactor pressure (PI-3) to determine inlet partial pressures*.

The experimental outlet compositions were determined similarly, except that the analysis pressure was taken as the arithmetic average between differential reactor outlet (PI-4) and chromatograph outlet (PI-5). After mol fraction calculation, a new stoichiometrically exact set of outlet mol fractions was synthesized from the inlet compositions plus the outlet CH_4 composition[2]. The synthesized values were printed next to the experimental values for easy comparison. Generally the values agreed within a factor of 1%, and often the agreement was much better. Constituent outlet partial pressures* were then calculated from the synthesized outlet composition and outlet reactor pressure.

<u>Reactor Flow Rates</u> - Laminar flowmeter voltages were converted to total volumetric inlet flow* and then weight flow (lb/hr) using flowmeter pressure, temperature, and the perfect gas laws. Volumetric flow rates for each constituent were then

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[1]Complete raw data is given in Reference 5, which is the NASA report of this work.
*Presented in Table 1 for all reported test runs.
[2]This was done to avoid errors in later calculations due to experimental inaccuracies.

calculated at reactor inlet and outlet, taking into account the reactor tempera-
ture*, pressure, and chromatographically determined compositions while conserving
only the total weight flow of the feed constituents. Contact time (sec) and space
velocity* (1/hr) were calculated using the reactor volume* and average reactor flow
rate. Reactor inlet and outlet flows in lb-mols/hr were then calculated, using
volumetric flows and the perfect gas laws.

Reaction Rates - Molar CO_2 reaction rate (lb-mol/hr) was then calculated from the
difference in inlet and outlet molar flow rates of CO_2. Then the specific conver-
sion rate was calculated (lb-mol/hr catalyst), using catalyst weight*.

CO_2 reaction rate* in atm/hr was also calculated, using the perfect gas law
at reaction conditions and the molar reaction rate.

DATA CORRELATION

Reduced run data listed in Table I was further processed to determine values
of the activation energy, Ea, catalyst coefficient, n, and reaction rate coeffi-
cient, k.

Activation Energy and Catalyst Coefficient - A specail computer program was written
to process reduced data from the activation energy runs to a form appropriate for
graphically fitting equation (7). A least squares fit was incorporated to calcu-
late the activation energy directly. Table II is an output from this program for
n = 1/4. The data were fitted using catalyst coefficients of n = 1/4, 3/8, 1/2,
and 1. When n was 1/4 or 3/8, a plot of equation (7) was generally linear (Figures
7 and 8). The data were more linear with n = 1/4 and this was selected as the
catalyst coefficient, resulting in a value for activation energy of

Ea = 30,600		btu/lb mols CO_2
or		
Ea = 17.0		Kcal/g mols CO_2

Rate Coefficient - Table III is the output from the Runge-Kutta integration
routine which calculates the rate constants for selected runs according to
equation (11). Data for integration were selected as noted in Table IV.

The required program input for the data reduction is tabulated along with
the calculated rate constant for each run. The average constant is

$$k = 2.46 \times 10^9 \text{ atm}^{-1/4} \text{ hr}^{-1}$$

for the constant temperature runs 544.1 to 581.0 and

$$k = 2.338 \times 10^9 \text{ atm}^{-1/4} \text{ hr}^{-1}$$

for the entire page of tests of Table IV.

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*Presented in Table I for all reported test runs.

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Table I
SUMMARY OF EXPERIMENTAL DATA AFTER PRELIMINARY PROCESSING
3.58 GRAMS CATALYST USED IN 4.15 ML REACTOR
INLET/OUTLET PARTIAL PRESSURES SUM TO INLET/OUTLET TOTAL PRESSURE
SPACE VELOCITY AND PCO2 CONSUMED CALCULATED AT REACTOR TEMP AND PRESSURE
INLET FLOW (CUBIC FT/HR) MEASURED AT 19 PSIA AND 73 DEG F
CATALYST COEFFICIENT = 0.25

TEST NUMBER	ABSCISSA X(NP) (1/DEG R)	URDINATE Y(NP)	REACTOR TEMP. (DEG.F)	WALL TEMP (DEG F)	PCO2 CONSUMED (ATM/HR)	SPACE VELOCITY (1/HR)	INLET FLOW (CFH)	INLET CO2 (ATM)	OUTLET CO2 (ATM)	INLET H2 (ATM)	OUTLET H2 (ATM)	INLET H2O (ATM)	OUTLET H2O (ATM)	INLET CH4 (ATM)	OUTLET C44 (ATM)
519.00	0.001157	3.4184	404.	404.	16.380	1520.	0.2117	0.2036	0.2002	0.8033	0.7984	0.0	0.0115	0.0	0.0058
520.00	0.001120	4.1264	433.	433.	32.730	1548.	0.2117	0.1978	0.1911	0.8091	0.7828	0.0	0.0220	0.0	0.0110
520.10	0.00112C	4.0221	433.	433.	29.810	2877.	0.4172	0.2047	0.2015	0.8022	0.7893	0.0	0.0107	0.0	0.0054
521.00	0.00110C	4.2811	443.	443.	38.510	2878.	0.4169	0.2034	0.1993	0.8035	0.7870	0.0	0.0137	0.0	0.0069
521.10	0.001069	5.1155	462.	462.	86.250	3874.	0.4172	0.1386	0.1305	0.8683	0.8427	0.0	0.0225	0.0	0.0112
521.40	0.001076	4.8554	469.	469.	67.830	3058.	0.4239	0.2036	0.1970	0.8034	0.7767	0.0	0.0222	0.0	0.0111
522.30	0.001036	5.6127	505.	505.	141.000	3021.	0.4243	0.2055	0.1899	0.8050	0.7422	0.0	0.0453	0.0	0.0226
523.30	0.001042	5.5438	500.	500.	105.500	2792.	0.4256	0.1714	0.1575	0.6814	0.6257	0.1060	0.1454	0.0517	0.0714
524.00	0.001013	5.7263	527.	52C.	127.430	2703.	0.4231	0.1790	0.1645	0.6818	0.6224	0.0987	0.1480	0.0475	0.0721
525.10	0.000986	6.2092	552.	543.	199.600	2670.	0.4231	0.1799	0.1573	0.6826	0.5856	0.0968	0.1739	0.0476	0.0981
525.10	0.000995	6.0728	545.	537.	175.500	2671.	0.4231	0.1799	0.1600	0.6800	0.5979	0.0994	0.1575	0.0475	0.0316
526.00	0.000987	5.9528	553.	548.	115.200	2415.	0.4231	0.1487	0.1331	0.5370	0.4721	0.2141	0.2678	0.1071	0.1340
527.00	0.000965	6.3181	576.	567.	157.000	2379.	0.4231	0.1485	0.1272	0.5298	0.4409	0.2197	0.2932	0.1090	0.1457
527.10	0.000981	6.0471	559.	551.	123.500	2393.	0.4231	0.1485	0.1316	0.5298	0.4595	0.2197	0.2778	0.1090	0.1383
527.20	0.000972	6.2076	569.	560.	142.500	2385.	0.4231	0.1485	0.1291	0.5298	0.4490	0.2197	0.2865	0.1090	0.1424
528.10	0.000943	6.7065	600.	587.	218.200	2355.	0.4227	0.1477	0.1181	0.5305	0.4071	0.2197	0.3217	0.1090	0.1500
529.20	0.000945	6.7426	598.	589.	171.000	2228.	0.4223	0.1243	0.0984	0.4362	0.3280	0.2665	0.3859	0.1499	0.1946
530.00	0.000923	7.1121	623.	612.	222.830	2187.	0.4223	0.1255	0.0916	0.4299	0.2878	0.3804	0.4178	0.1510	0.2097
531.00	0.000954	7.3570	652.	639.	252.600	2166.	0.4223	0.1229	0.0846	0.4202	0.2558	0.3059	0.4380	0.1579	0.2245
532.00	0.000954	7.4365	652.	648.	64.010	1928.	0.4223	0.0714	0.0594	0.1805	0.1298	0.5023	0.5441	0.2526	0.2735
533.00	0.000860	7.7548	677.	670.	66.850	1927.	0.4223	0.0714	0.0592	0.1805	0.1287	0.5023	0.5450	0.2526	0.2740
534.00	0.000862	8.2982	700.	694.	73.170	1925.	0.4223	0.0714	0.0582	0.1805	0.1248	0.5023	0.5482	0.2526	0.2755
536.50	0.001163	3.4621	400.	400.	14.520	2836.	0.4352	0.3893	0.3874	0.6175	0.6076	0.0	0.0055	0.0	0.0027
539.50	0.001133	3.9847	423.	423.	26.910	2582.	0.4063	0.3414	0.3374	0.6654	0.6463	0.0	0.0129	0.0	0.0054
540.10	0.001124	4.1073	430.	430.	29.730	2567.	0.4063	0.3435	0.3393	0.6633	0.6427	0.0	0.0129	0.0	0.0060
540.20	0.001111	4.2998	440.	440.	36.660	2564.	0.4063	0.3435	0.3388	0.6633	0.6342	0.0	0.0147	0.0	0.0073
540.80	0.001094	4.5448	450.	450.	46.630	2559.	0.4063	0.3435	0.3382	0.6633	0.6340	0.0	0.0195	0.0	0.0093
541.10	0.001056	5.1762	485.	480.	86.020	2527.	0.4063	0.3455	0.3379	0.6613	0.6117	0.0	0.0336	0.0	0.0168
541.12	0.001056	5.1668	485.	480.	85.250	2528.	0.4063	0.3455	0.3380	0.6613	0.6121	0.0	0.0333	0.0	0.0166
542.00	0.001053	5.1734	490.	485.	85.980	2555.	0.4070	0.3434	0.3359	0.6634	0.6146	0.0	0.0330	0.0	0.0165
542.10	0.001036	5.5472	505.	498.	123.300	2538.	0.4070	0.3434	0.3336	0.6634	0.5945	0.0	0.0472	0.0	0.0236
543.00	0.001047	5.5149	495.	491.	55.830	2284.	0.4070	0.3305	0.3264	0.5117	0.4782	0.1051	0.1314	0.0595	0.0728
544.00	0.001029	5.5951	512.	505.	96.920	2263.	0.4070	0.3312	0.3241	0.5124	0.4567	0.1081	0.1539	0.0552	0.0781
544.10	0.001020	5.6702	520.	514.	103.900	2260.	0.4070	0.3312	0.3236	0.5124	0.4446	0.1081	0.1570	0.0552	0.0797
544.20	0.001012	5.6089	526.	521.	141.600	2243.	0.4070	0.3312	0.3208	0.5124	0.4221	0.1081	0.1752	0.0552	0.0898
544.30	0.001006	6.0740	534.	525.	150.100	2240.	0.4070	0.3312	0.3202	0.5124	0.4170	0.1081	0.1790	0.0552	0.0907
545.00	0.001021	5.6147	519.	512.	85.050	2151.	0.4070	0.3302	0.3226	0.4476	0.3872	0.1543	0.1973	0.0782	0.0997
545.10	0.001012	5.7134	528.	519.	93.110	2153.	0.4073	0.3302	0.3220	0.4476	0.3822	0.1543	0.2010	0.0782	0.1016
545.30	0.001010	6.6705	534.	524.	107.420	2141.	0.4070	0.3302	0.3209	0.4476	0.3722	0.1543	0.2085	0.0782	0.1053
546.10	0.000999	6.0206	541.	532.	121.530	2145.	0.4078	0.3276	0.3192	0.4427	0.3593	0.1547	0.2226	0.0779	0.1288
547.10	0.000969	6.5732	572.	558.	194.800	2106.	0.4070	0.3275	0.3125	0.4428	0.3086	0.1543	0.2578	0.0783	0.1280
548.00	0.000960	6.0161	560.	559.	56.320	1884.	0.4070	0.2647	0.2581	0.1527	0.1021	0.3941	0.4320	0.2024	0.2215
549.00	0.000955	6.9452	587.	581.	69.570	1879.	0.4070	0.2647	0.2568	0.1526	0.0914	0.3941	0.4472	0.2024	0.2755
549.10	0.000998	6.9998	590.	581.	133.500	1929.	0.4070	0.2865	0.2729	0.2477	0.1379	0.3164	0.3984	0.1632	0.2745
550.00	0.000929	7.3386	616.	604.	167.500	1922.	0.4070	0.2855	0.2686	0.2502	0.1146	0.3154	0.4167	0.1627	0.2137
551.00	0.000909	7.6399	640.	628.	196.500	1907.	0.4066	0.2855	0.2659	0.2494	0.0916	0.3161	0.4342	0.1627	0.2221
560.00	0.000923	7.4629	624.	589.	629.500	2327.	0.4067	0.3417	0.2998	0.6686	0.3320	0.0	0.2590	0.0	0.1295
561.00	0.000935	7.2606	610.	568.	365.200	2110.	0.4067	0.3237	0.2943	0.4848	0.2412	0.1375	0.3184	0.0663	0.1563
562.00	0.000942	7.1130	602.	583.	270.100	2045.	0.4059	0.3151	0.2923	0.4143	0.2214	0.1865	0.3352	0.0944	0.1564
563.00	0.000947	7.0640	596.	581.	210.000	1998.	0.4059	0.3017	0.2824	0.3468	0.1860	0.2400	0.3587	0.1217	0.1313
564.00	0.000954	7.0509	588.	578.	131.100	1914.	0.4059	0.2855	0.2721	0.2362	0.1268	0.3214	0.4031	0.1638	0.2048
565.00	0.000954	6.8468	568.	579.	131.900	2004.	0.4321	0.1708	0.1509	0.3028	0.2014	0.3542	0.4340	0.1803	0.2204
566.00	0.000950	7.1900	593.	579.	215.200	1987.	0.4321	0.1960	0.1654	0.3599	0.1964	0.3248	0.4556	0.1274	0.1994
567.00	0.000945	6.9837	598.	580.	277.800	2183.	0.4321	0.2143	0.1800	0.4990	0.3213	0.1991	0.3372	0.0938	0.1684
568.00	0.000943	7.0545	601.	580.	346.000	2269.	0.4321	0.2258	0.1860	0.5672	0.3622	0.1456	0.3566	0.0717	0.1521
569.00	0.000929	7.3290	617.	583.	618.700	2508.	0.4321	0.2600	0.2027	0.7482	0.4515	0.0	0.2351	0.0	0.1175
570.00	0.001009	6.0666	531.	520.	201.900	2632.	0.4311	0.2623	0.2436	0.7514	0.6561	0.0	0.0717	0.0	0.0369
571.00	0.001013	5.6610	527.	52C.	122.000	2317.	0.4311	0.2226	0.2078	0.5567	0.4820	0.1567	0.2162	0.0776	0.1063
572.00	0.001014	5.6642	526.	519.	68.950	2301.	0.4311	0.2011	0.1887	0.5043	0.4459	0.2052	0.2479	0.1030	0.1244
573.00	0.001021	5.7880	519.	520.	80.190	2139.	0.4311	0.1924	0.1807	0.4514	0.3571	0.2042	0.3136	0.1307	0.1589
574.00	0.001016	6.3864	524.	520.	107.300	2037.	0.4311	0.1755	0.1584	0.3404	0.2555	0.3303	0.3965	0.1670	0.1999
575.00	0.001016	5.7722	524.	520.	46.150	1978.	0.4311	0.1604	0.1523	0.2654	0.2243	0.3895	0.4196	0.1944	0.2131
576.00	0.001013	5.9192	527.	520.	62.320	2026.	0.4082	0.2828	0.2755	0.2692	0.2179	0.3063	0.3430	0.1554	0.1738
577.00	0.001012	5.7083	528.	520.	73.800	2133.	0.4082	0.3000	0.2923	0.3700	0.3153	0.2288	0.2591	0.1145	0.1345
578.00	0.001011	5.7293	529.	520.	90.350	2211.	0.4082	0.3089	0.3033	0.4350	0.3728	0.1806	0.2255	0.0890	0.1115
579.00	0.001005	5.5664	529.	521.	144.500	2352.	0.4082	0.3223	0.3106	0.5442	0.4566	0.0093	0.1614	0.0474	0.0798
580.00	0.001010	5.8392	530.	520.	151.030	2501.	0.4082	0.3306	0.3195	0.6270	0.5453	0.0186	0.0943	0.0175	0.0473
581.00	0.001009	5.5403	531.	52C.	184.600	2620.	0.4558	0.3377	0.3253	0.6760	0.5827	0.0	0.0675	0.0	0.0337
590.00	0.001117	4.5419	435.	0.	49.620	3067.	0.4267	0.1954	0.1889	0.8115	0.7860	0.0	0.0167	0.0	0.0084
591.00	0.001070	5.1849	475.	470.	43.130	3047.	0.4267	0.1954	0.1847	0.8115	0.7696	0.0	0.0304	0.0	0.0152

TABLE II

ACTIVATION ENERGY FROM SERIES 500 TESTS—8/19/78—CO2=.25 H2=1.0—NEW CALIB. CURVES

TEST NUMBER	ABSCISSA X(NP) (1/DEG R)	ORDINATE Y(NP)	REACTOR TEMP. (DEG F)	PCO2 CONSUMED (ATM/HR)	SPACE VELOCITY (1/HR)	INLET CO2 (ATM)	OUTLET CO2 (ATM)	INLET H2 (ATM)	OUTLET H2 (ATM)	INLET H2O (ATM)	OUTLET H2O (ATM)	INLET CH4 (ATM)	OUTLET CH4 (ATM)
519.00	.001180	4.1264	433.	32.730	1946.	.1070	.1911	.8091	.7826	.0000	.0220	.0000	.0110
520.10	.001120	4.0221	433.	29.810	2077.	.2047	.2015	.8022	.7893	.0000	.0107	.0000	.0054
521.00	.001107	4.2811	443.	38.510	2078.	.2034	.1993	.8035	.7870	.0000	.0137	.0000	.0069
521.10	.001085	5.1155	462.	64.250	3074.	.1586	.1305	.8603	.8427	.0000	.0225	.0000	.0112
521.40	.001076	4.8554	469.	67.830	3050.	.2036	.1070	.8034	.7767	.0000	.0222	.0000	.0111
522.30	.001036	5.6127	505.	141.000	3021.	.2053	.1899	.8050	.7422	.0000	.0453	.0000	.0226
523.30	.001042	5.5439	500.	105.500	2792.	.1714	.1575	.6014	.6257	.1060	.1454	.0517	.0714
524.00	.001013	5.7263	527.	127.400	2703.	.1790	.1645	.6018	.6224	.0987	.1480	.0475	.0721
525.00	.000986	6.2092	552.	199.400	2070.	.1799	.1573	.6026	.5896	.0968	.1739	.0476	.0841
525.10	.000995	6.0728	545.	175.300	2671.	.1799	.1600	.6000	.5979	.0994	.1675	.0476	.0816
526.00	.000987	5.9520	553.	115.200	2415.	.1487	.1331	.5370	.4721	.2141	.2678	.1071	.1340
527.00	.000965	6.3181	576.	157.800	2379.	.1485	.1272	.5298	.4409	.2197	.2932	.1090	.1457
527.10	.000981	6.0471	559.	123.500	2393.	.1485	.1316	.5298	.4595	.2197	.2778	.1090	.1380
527.20	.000972	6.2076	569.	142.500	2385.	.1485	.1291	.5298	.4490	.2197	.2865	.1090	.1424
528.10	.000943	6.7065	600.	218.200	2355.	.1477	.1181	.5305	.4071	.2197	.3217	.1090	.1600
529.20	.000945	6.7420	598.	171.000	2228.	.1203	.0984	.4362	.3280	.2965	.3859	.1499	.1946
530.00	.000923	7.1121	623.	222.800	2107.	.1255	.0916	.4299	.2878	.3004	.4170	.1510	.2097
531.00	.000899	7.3570	652.	252.400	2166.	.1229	.0846	.4202	.2598	.3059	.4340	.1579	.2245
532.00	.000898	7.4385	652.	64.010	1928.	.0714	.0594	.1805	.1298	.5023	.5441	.2526	.2735
533.00	.000880	7.7548	677.	66.450	1927.	.0714	.0592	.1805	.1287	.5023	.5450	.2526	.2740
534.00	.000862	8.2982	700.	73.170	1925.	.0714	.0582	.1805	.1248	.5023	.5482	.2526	.2756
538.50	.001163	3.4021	400.	14.520	2836.	.3493	.3474	.6175	.6078	.0000	.0055	.0000	.0027
539.50	.001133	3.9848	423.	26.910	2562.	.3414	.3374	.6654	.6463	.0000	.0109	.0000	.0054
540.10	.001126	4.0873	430.	29.730	2567.	.3435	.3393	.6633	.6427	.0000	.0120	.0000	.0060
540.20	.001111	4.2998	440.	36.680	2564.	.3435	.3388	.6633	.6392	.0000	.0147	.0000	.0073
540.80	.001099	4.5448	450.	46.430	2580.	.3435	.3382	.6633	.6340	.0000	.0165	.0000	.0093
541.10	.001056	5.1762	485.	86.020	2527.	.3455	.3379	.6613	.6117	.0000	.0336	.0000	.0168
541.12	.001056	5.1068	485.	85.250	2528.	.3455	.3380	.6613	.6121	.0000	.0333	.0000	.0166
542.00	.001053	5.1734	490.	85.980	2555.	.3434	.3359	.6634	.6146	.0000	.0330	.0000	.0165
542.10	.001034	5.5506	505.	123.300	2538.	.3434	.3336	.6634	.5955	.0000	.0472	.0000	.0236
543.00	.001047	5.2149	495.	55.430	2284.	.3305	.3264	.5117	.4762	.1051	.1314	.0595	.0728
544.00	.001029	5.5951	512.	96.920	2263.	.3312	.3241	.5124	.4507	.1081	.1539	.0552	.0701
544.10	.001020	5.6702	520.	163.500	2260.	.3312	.3236	.5124	.4466	.1081	.1570	.0552	.0797
544.20	.001012	6.0089	526.	181.400	2243.	.3312	.3208	.5124	.4221	.1081	.1752	.0552	.0888
544.30	.001006	6.0749	534.	150.100	2240.	.3312	.3202	.5124	.4170	.1081	.1790	.0552	.0907
545.00	.001021	5.6147	519.	85.050	2151.	.3302	.3226	.4476	.3872	.1543	.1973	.0782	.0997
545.10	.001012	5.7134	526.	93.110	2133.	.3302	.3220	.4476	.3822	.1543	.2010	.0782	.1016
545.30	.001006	5.8705	534.	107.400	2141.	.3302	.3209	.4476	.3722	.1543	.2085	.0782	.1053
546.10	.000999	6.0206	541.	121.300	2145.	.3276	.3182	.4427	.3563	.1587	.2206	.0779	.1088
547.00	.000969	6.5732	572.	194.800	2106.	.3275	.3125	.4428	.3086	.1583	.2578	.0783	.1280
548.00	.000966	6.6161	568.	56.320	1884.	.2647	.2581	.1527	.1021	.3941	.4320	.2024	.2215
549.00	.000956	6.9452	587.	69.570	1879.	.2647	.2568	.1528	.0914	.3941	.4400	.2024	.2255
549.10	.000952	6.9996	590.	133.500	1929.	.2665	.2729	.2477	.1379	.3164	.3984	.1632	.2045
550.00	.000929	7.3386	616.	167.500	1922.	.2655	.2686	.2582	.1146	.3154	.4167	.1627	.2137
551.00	.000909	7.6599	640.	196.500	1987.	.2655	.2659	.2594	.0916	.3161	.4342	.1627	.2221

EQUATION FOR ACTIVATION ENERGY IS
LOG(RATE/(C-O)) = LOG(K) - (EACT/RT), WHERE (C-O) = F(PCO2, PH2, PH2O, PCH4, KFQ)

ACT. ENERGY = .30593+05 AND INTERCEPT = .2141+02

TABLE III

RATE CONSTANT FROM SERIES 500 TESTS—8/28/78—CO2=.25 H2=1.0—NEW CALIB. CURVES. DATE 08/28/78 TIME

FORWARD RATE CONSTANT OF SABATIER REACTION BY RUNGE-KUTTA INTEGRATION

TEST NUMBER	RATE CONSTANT (1/HR-ATM**5)	REACTOR TEMP. (DEG F)	SPACE VELOCITY (1/HR)	ACTIVATION ENERGY (BTU/LB-MOLE CO2)	PCO2 CONSUMED (ATM)	INLET CO2 (ATM)	INLET H2 (ATM)
519.0	.17864+10	433.	1946.	30593.	.0187	.2034	.8033
520.0	.08130+10	433.	1940.	30593.	.0211	.1978	.8041
520.1	.17787+10	433.	2077.	30593.	.0186	.2047	.8022
521.0	.19120+10	443.	2078.	30593.	.0130	.2034	.8035
521.1	.31784+10	462.	3074.	30593.	.0273	.1586	.8603
521.4	.21830+20	469.	3050.	30593.	.0272	.2036	.8034
522.3	.06307+10	505.	3021.	30593.	.0467	.2053	.8050
523.3	.26801+10	500.	2792.	30593.	.0378	.1714	.6014
524.0	.21320+10	527.	2703.	30593.	.0477	.1790	.6018
525.0	.26603+10	552.	2070.	30593.	.0798	.1799	.6026
525.1	.24727+10	545.	2671.	30593.	.0659	.1799	.6000
526.0	.18876+10	553.	2415.	30593.	.0479	.1487	.5370
527.0	.22025+10	576.	2379.	30593.	.0661	.1485	.5298
527.1	.19810+10	559.	2393.	30593.	.0516	.1485	.5298
527.2	.20742+10	569.	2385.	30593.	.0597	.1485	.5298
528.1	.31230+10	600.	2355.	30593.	.0908	.1477	.5305
538.5	.17882+10	400.	2836.	30593.	.0050	.3493	.6175
539.5	.20640+10	423.	2562.	30593.	.0106	.3414	.6654
540.1	.20083+10	430.	2567.	30593.	.0116	.3435	.6633
540.2	.20606+10	440.	2564.	30593.	.0143	.3435	.6633
540.8	.22006+10	450.	2580.	30593.	.0182	.3435	.6633
541.1	.23220+10	485.	2527.	30593.	.0341	.3455	.6613
541.1	.22918+10	485.	2528.	30593.	.0337	.3455	.6613
542.0	.21220+10	490.	2555.	30593.	.0337	.3434	.6634
542.1	.25358+10	505.	2538.	30593.	.0484	.3434	.6634
543.0	.16463+10	495.	2284.	30593.	.0294	.3305	.5117
544.0	.23874+10	512.	2263.	30593.	.0427	.3312	.5124
544.1	.23070+10	520.	2260.	30593.	.0448	.3312	.5124
544.2	.31235+10	526.	2243.	30593.	.0631	.3312	.5124
544.3	.31272+10	534.	2240.	30593.	.0671	.3312	.5124
545.0	.21980+10	519.	2151.	30593.	.0396	.3302	.4476
545.1	.21412+10	526.	2133.	30593.	.0432	.3302	.4476
545.3	.13003+10	534.	2141.	30593.	.0588	.3302	.4476
546.1	.26120+10	541.	2145.	30593.	.0666	.3276	.4427
570.0	.28758+10	531.	2632.	30593.	.0768	.2025	.7510
571.0	.25637+10	527.	2317.	30593.	.0570	.2826	.5587
572.0	.19815+10	526.	2341.	30593.	.0378	.2011	.5003
573.0	.20461+10	519.	2139.	30593.	.0375	.1924	.8152
575.0	.23087+10	524.	1974.	30593.	.0834	.1600	.7650
576.0	.27776+10	527.	2036.	30593.	.0307	.2828	.7677
577.0	.20786+10	528.	2132.	30593.	.0381	.4000	.7700
578.0	.21363+10	520.	2211.	30593.	.0809	.4000	.8300
579.0	.20678+10	529.	2342.	30593.	.0615	.4273	.4662
580.0	.23080+10	530.	2501.	30593.	.0606	.3306	.4879
581.0	.27150+10	531.	2620.	30593.	.0780	.4377	.4760

STANDARD DEVIATION OF ABOVE RATE CONSTANTS = .3007+09

TABLE IV - Selection of Experimental Data

Selection of runs for activation energy determination
(Table II, Figures 7 and 8)

<u>Reason</u>

Planned: Runs 519 - 551
Dropped: Run 519   Reaction rate so low that analyses
were in doubt
Used: Runs 520 - 551

Selection of runs for rate constant determination
(Table III)

Planned: Runs 560 - 581
Dropped: Runs 560 - 569   High difference between wall and
(entire 580°   reactor temperatures due to generally
bath temperature high conversions caused doubt as to
series)   actual reaction temperature.
Added: Runs 519 - 528.1 Lower temperature runs from activation
538.5 - 546.1   energy series replaced above data.
Used: Runs 519 - 528.1
538.5-546.1
570 - 581

Runs 590 and 591 were extra runs not planned and not used.

FIGURE 1   THERMODYNAMIC EQUILIBRIA FOR THE SABATIER REACTION
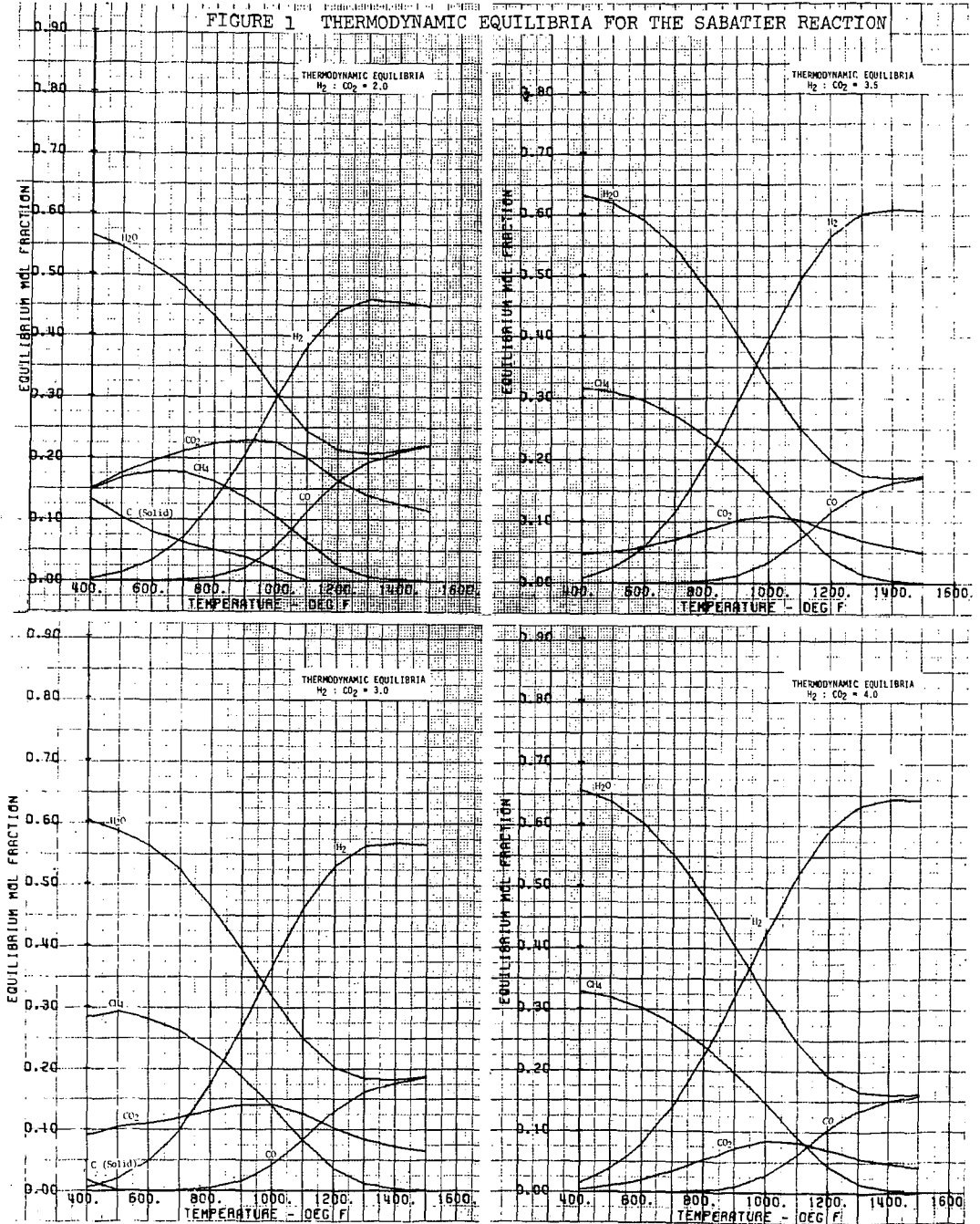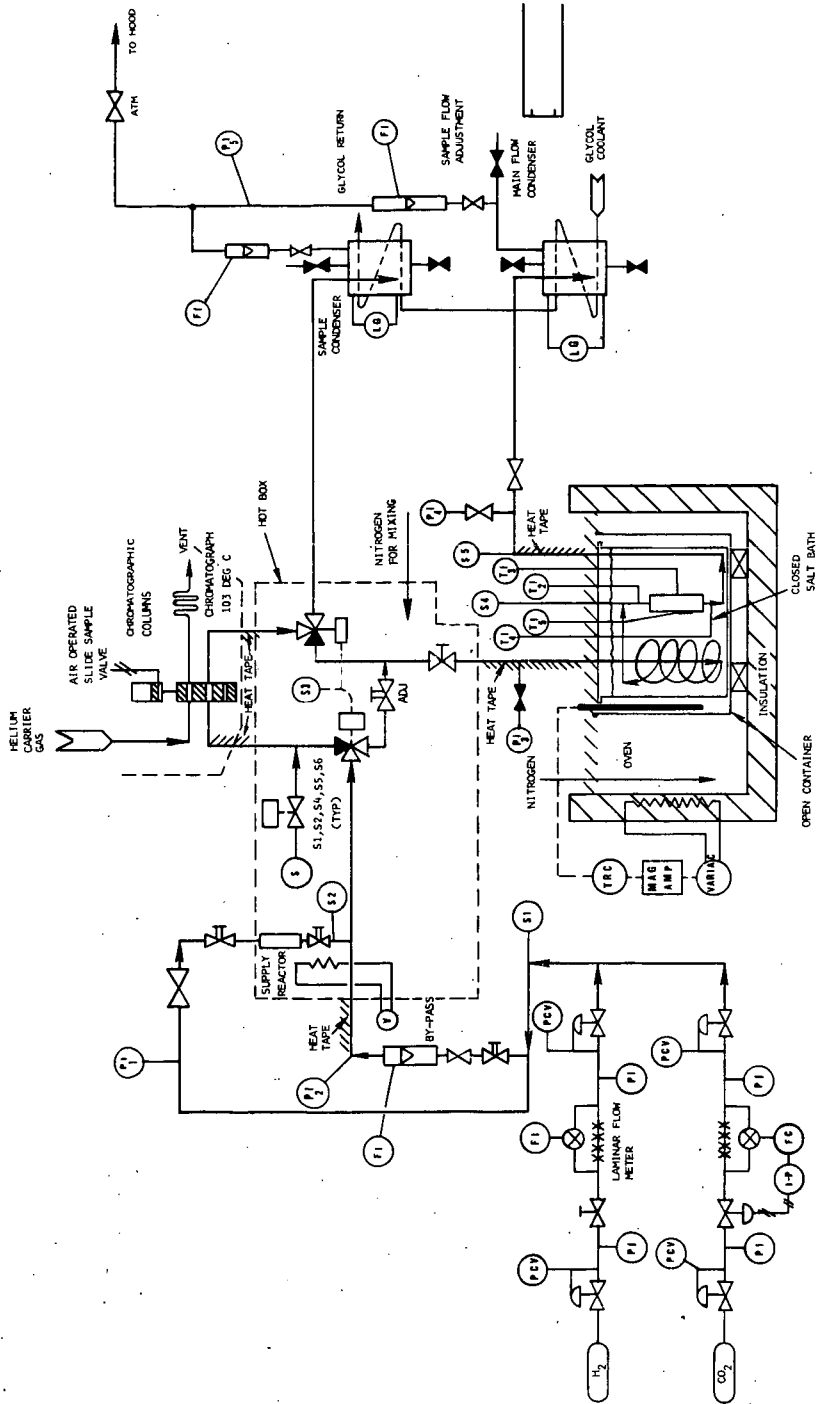
FIGURE 2. RATE DATA APPARATUS, SABATIER REACTION
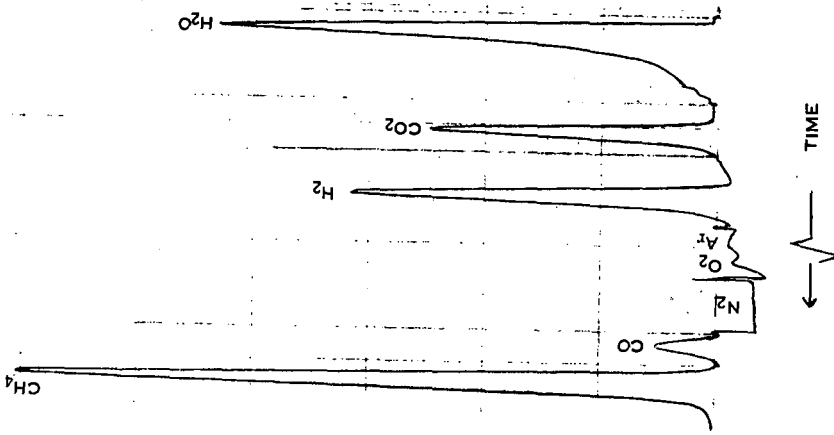
FIGURE 4   CHROMATOGRAPHIC TRACE
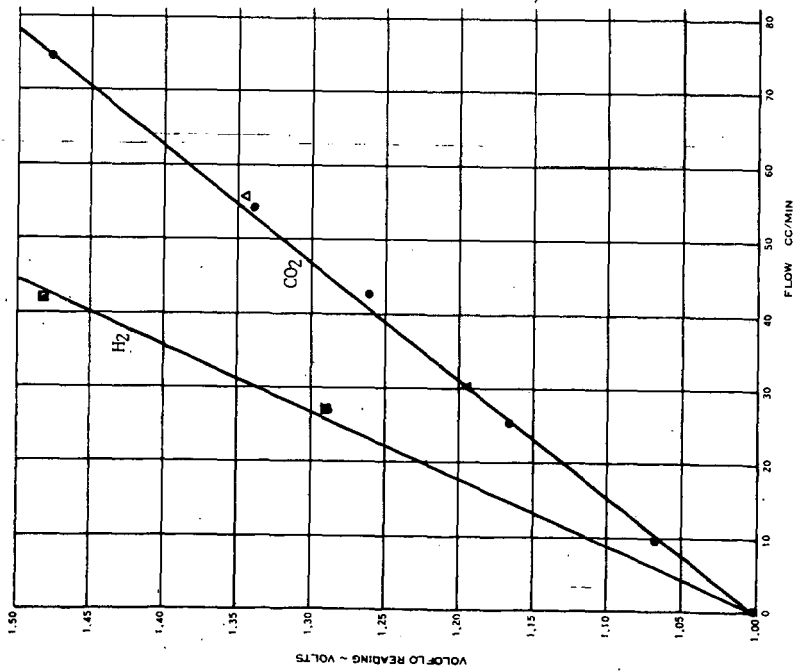
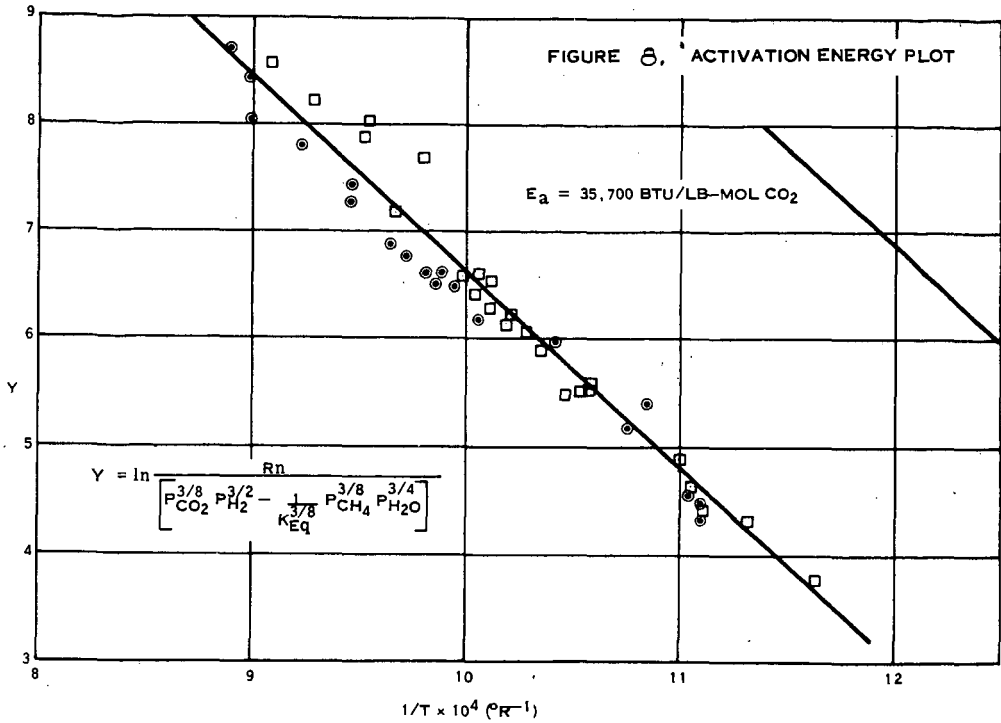
FIGURE 3   VOLOFLO CALIBRATION CURVE FOR CO_2 AND H_2
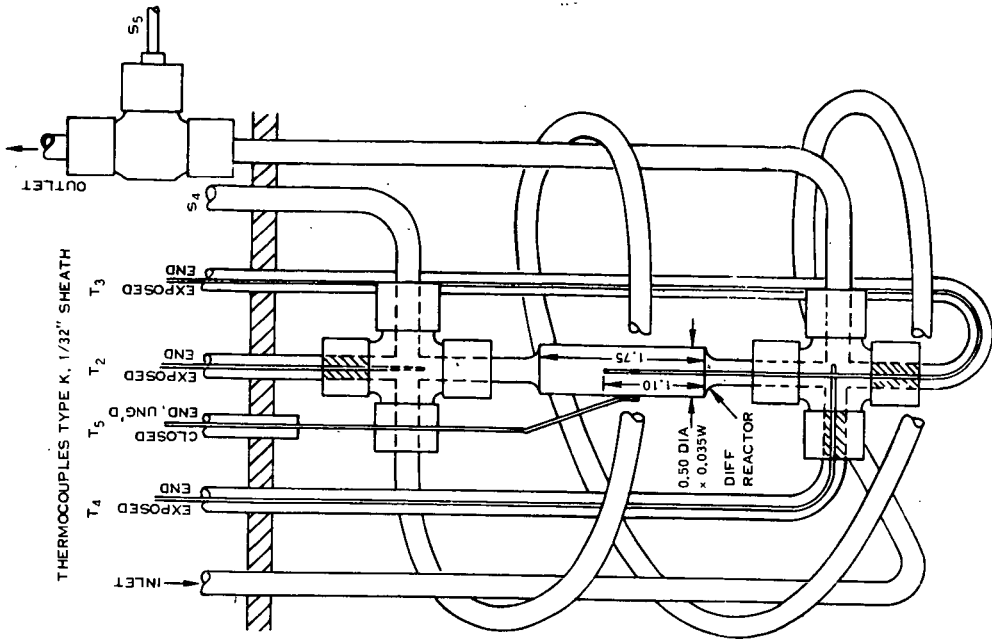
FIGURE 6 TEST REACTOR SABATIER

FIGURE 5 CHROMATOGRAPH CALIBRATIONS

FIGURE 8. ACTIVATION ENERGY PLOT

$E_a = 35,700$ BTU/LB–MOL CO_2

$$Y = \ln \frac{Rn}{\left[P_{CO_2}^{3/8}\, P_{H_2}^{3/2} - \frac{1}{K_{Eq}^{3/8}}\, P_{CH_4}^{3/8}\, P_{H_2O}^{3/4} \right]}$$

$1/T \times 10^4\ (°R^{-1})$

FIGURE 7. ACTIVATION ENERGY PLOT

$E_a = 30,593$ BTU/LB. MOL CO_2

$$Y = \ln \frac{Rn}{\left[P_{CO_2}^{1/4}\, P_{H_2} - \frac{1}{K_{Eq}^{1/4}}\, P_{CH_4}^{1/4}\, P_{H_2O}^{1/2} \right]}$$

$1/T \times 10^4\ (°R^{-1})$
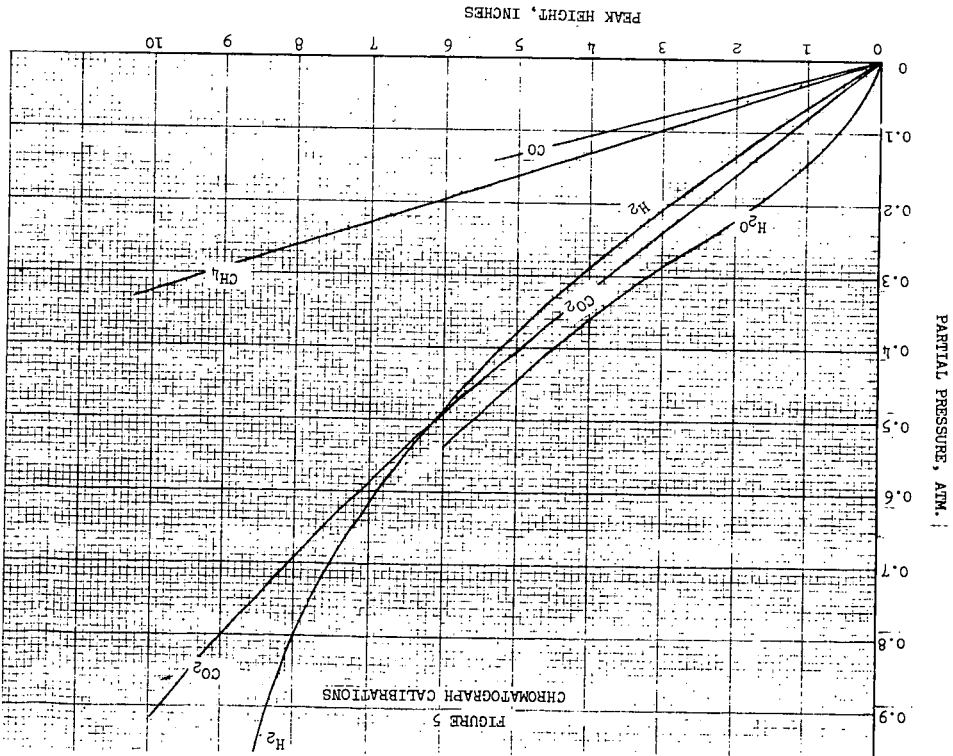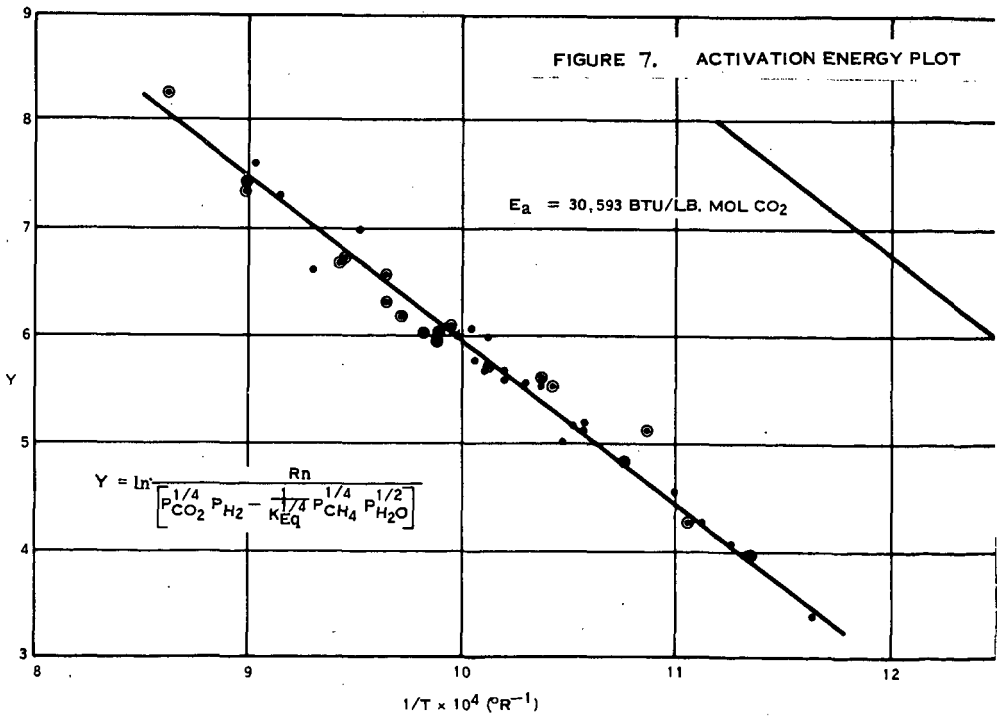
Coal Hydrogenation in Small Tube Reactors

R. E. Wood and G. R. Hill

Department of Mining, Metallurgy and Fuels Engineering
University of Utah
Salt Lake City, Utah

The office of Coal Research short residence time coal hydrogenation reactor at the University of Utah has been previously discussed in Hydrocarbon Processing[1] and The Quarterly of the Colorado School of Mines[2].

A schematic diagram of this device is shown in Figure 1. It contains provision for passing dry powdered coal through a heated and pressurized reaction zone. The reactor is mounted vertically and the coal is pushed by means of an auger feeder into the top and the reaction products are collected in a water cooled quench tank at the bottom. This reactor can be pressurized to 5000 PSI and heated to 800°C.

Although conversions to 75 or 80 percent of the coal matter can be realized in this apparatus, it suffers from some rather crippling deficiencies. Of greatest importance in limiting the usefulness of the device is the fact that coal, in falling through the reaction zone becomes plastic and sticky. Some of the liquid-solid product sticks to the reactor walls, becomes devolitilized and the residue remains as a solid char that builds up to eventually block the passage. A second factor is that the limited capacity of the compressor (240 cubic feet per hour maximum) severely restricts the movement of gas through the reaction zone. This essentially stagnant reactor space contributes to the coal and char sticking problem as there is little flow of gas to force the solid material through to the quench vessel.

Calculations of Reynolds numbers for hydrogen at 2000 PSI and 700°C reveals that a flow of 200 cubic feet perhour will not provide turbulent flow in tubes larger than 3/16 inch I.D. Therefore, we restricted the reactor tube size to 1/8 inch and proceeded to work with hydrogen-coal slurries in this type of reactor.

The auger feeder used with the 2 inch I.D. reactor is not adaptable to the 1/8 inch tube because it delivers coal in slugs rather than at a steady rate. The small tube is blocked by each slug of coal delivered by the auger. For this reason a fluidized feeder, where hydrogen gas passing through a coal bed carries the coal into the small tube reactor was developed. The design of this feeder, with the small tube reactor is indicated in Figure 3. This schematic shows the 1/8 inch tube mounted inside the 2 inch tube of the original reactor. This construction adds a further factor in that heat to raise the coal to reaction temperature must be added from outside the 2 inch reactor. Convection and radiation from the inner wall of the larger reactor is insufficient to heat the small tube enough to permit it in turn to properly heat the coal-hydrogen stream passing through it. Therefore, a chamber was constructed around the inner tube such that a molten lead bath could be used to transmit heat from the walls of the outer tube to the inner reactor.

Figure 4 shows the product distribution, in terms of gases and liquids, produced as a function of temperature and pressure for one of the more reactive coal types. This is Orangeville, Utah, coal, a high-volatile bituminous "B" coal from East Central Utah. The production of gases, primarily Methane but with substantial quantities of ethane, propane and higher carbon number hydrocarbon gases; and liquids, a very complicated mixture of aliphatic and aromatic materials is shown at four temperatures and three pressures. Increasing temperature increases the output of both gases and liquids, but the liquids are increased to a greater extent. Increased pressure likewise increases the production of liquids. Above 2000 PSI the gas production is decreased to some extent. The total conversion, equal to the sum of gases

plus liquids is over 60 percent of the original coal material at 675°C and 2000 PSI.

Table I is a compilation of data obtained on several different coals in this small tube reactor. Since these samples were measured over a period of several months, the reaction conditions were not completely uniform. Most were obtained at 1750 PSI hydrogen pressure and 650°C temperature, but some were measured at 675°C and 2000 PSI. The conditions were selected at less than a maximum conversion operation in an effort to spread the data to show coal differences. We have listed the coal, total conversion, feed rate, oxygen content and some observations about the coal. The coals are naturally broken into three categories. The first category contains those coals that are easy to feed and give little or no reactor plugging but which also give very little reaction. These are coals with high oxygen content and are generally of the lignite and subbituminous types. The second group of coals have an intermediate reaction, are not really difficult to feed, give some plugging and have an intermediate oxygen content. The third category of coals is generally the high volatile, non-caking bituminous coals that show good reaction without excessive plugging. Feeding with our hopper arrangement is difficult with these coals because they are sticky and agglomerate readily, particularly when the catalyst is present. This third group of coals is the most interesting because they react most readily. The conversions reported on these coals were obtained with half the catalyst application used with the other types. The lack of conversion numbers on some of these coals was because the higher level of catalyst was used and both feeding and plugging problems were encountered.

Table I. Comparison of Coals Treated in 1/8 inch I.D. reaction tube

| | Conversion | Feed Rate g/m | % O$_2$ | Coal Characteristic | | |
				Feeding	Reacting	Plugging
Sidney, Montana (Lignite)	11.1	19	21.0	GOOD	POOR	NONE
Big Horn, Wyoming	10.3	13	11.2	"	"	"
Navajo, Utah	17.5	14	----	"	"	"
Beluga River, Canada	17.9	10	28.3	"	"	"
Kanab, Utah	6.8	11	13.6	"	"	"
Alton, Utah	7.6	18	24.9	"	"	"
River King, Illinois	30.6	8	8.9	FAIR	FAIR	SOME
Last Chance, Utah	37.2	14	18.6	"	"	"
Kaiparowitz, Utah	45.0	--	18.0	"	"	"
Coalville, Utah	38.8	--	10.3	"	"	"
Powers, Utah	37.2	9	----	"	"	"
Geneva-Somerset, Utah-Colo.	48.4	14	6.4	POOR	GOOD	SOME
Spencer, Utah	44.1	9	12.3	"	"	"
Castle Valley, Utah	56.6	8	5.7	"	"	"
Orangeville, Utah	66.5	2	----	"	"	"
Hiawatha, Utah	76.8	8	----	"	"	"
Cedar City, Utah	----	--	7.5	"	"	"
Castle Gate, Utah	----	--	5.5	"	"	"
Coal Basin, Colorado	----	--	3.0	"	"	"
Bear, Colorado	----	--	8.5	"	"	"

Figure 5 shows the effect of changing catalyst concentration on two types of coal. The catalyst was zinc chloride and the application was measured in terms of weight of zinc metal to MAF coal. For Orangeville, Utah, coal, a good reacting material, the doubling of catalyst concentration accomplished little or nothing. For the Kaiparowitz coal, an intermediate reactor by our other standards, more catalyst gives a marked increase in conversion.

The coal feed rate is a process variable that is difficult to control with a fluidized feeder. It is affected by moisture content, concentration of catalyst, particle size and surface character of the coal particles. Figure 6 is an attempt to show the effect of both feed rate and particle size on the conversion in this process. The length of the horizontal lines indicate the mesh size range of the particles sample. The number by the line indicates the feed rate in grams of coal per minute. Two coals were studied. Kaiparowitz as shown in Figure 5 and Castle Gate, Utah, which is one of the better reacting type coals.

In general, we see that an increase in feed rate results in decreased reaction, presumably because of less efficient heating of larger quantities of coal to the required reaction condition. We see also that a decrease in particle size results in a decreased reaction. This is not to be expected because smaller coal particles should be heated more efficiently. The reason for this decreased reaction lies in the actual residence time of the coal within the heated zone. Because of the small size of the reactor, it has not been possible to insert probes, or even thermo-couples to measure residence times. However, we have been able to observe pressure buildup and decay as a small amount of coal is injected. We calculate that the gas is flowing at a rate where its residence in the hot zone is in the range of 0.01 to 0.03 seconds. However, the coal is traveling much less rapidly. Actually, it approaches a plug-flow condition. The pressure difference between top and bottom of the reactor tube increases as coal is injected and decays within 5-10 seconds. The coal residence then is somewhere in the range 1 to 10 seconds. This is somewhat dependent on particle size. The smaller particles tend to be carried with the gas and go through in less than 0.1 second. This is not long enough to heat even the finest particles enough to cause reaction. This, then is the reason for decreased reaction with a smaller particle size sample as indicated by the data of Figure 7.

The catalyst used in this work has been primarily $ZnCl_2$. It's action in the coal hydrogenation reaction is not understood although as a Lewis acid it is expected to act as a cracking catalyst for large organic molecules and the hydrogen reacts with the molecular fragments produced. Some studies have been made in an effort to discover the catalytically active form of the zinc and to devise schemes for recovering the zinc from the char for use on fresh coal. The economic success of the process will certainly depend on the almost complete recovery of this material.

Several kinds of inorganic materials have been tested as catalysts for this coal process. Table 2 shows the coal conversion obtained with each of these materials using the same coal and reaction conditions. Zinc halides and stannous chloride are the most effective of those tested. The zinc chloride is by far the cheaper material and therefore is the best selection.

Table 2. Comparison of Inorganic Salt Catalysts

Salt	Percent Conversion	Salt	Percent Conversion
$ZnBr_2$	58.5	Sn(powder)	7.9
ZnI_2	46.3	$CuCl_2.2H_2O$	7.6
$ZnCl_2$	41.1	$FeCl_3.6H_2O$	7.2
$SnCl_2 \cdot 2H_2O$	40.5	Zn(powder)	7.0
$SnCl_4 \cdot 5H_2O$	25.6	$ZnSO_4.7H_2O$	5.4
LiI	16.6	$(NH_4)_6Mo_7O_{24}.4H_2O$	5.4
$CrCl_3$	12.8	$FeCl_2$	3.3
$Pb(C_2H_3O_2)_2.3H_2O$	11.7	$CaCl_2.H_2O$	No Reaction
NH_4Cl	11.0	$Na_2CO_3.H_2O$	No Reaction
$CdCl_2.2\ 1/2\ H_2O$	7.9		

Conditions

Last Chance, Utah, Coal 40-100 mesh	Feed Rate 10-12 g/m
Pressure 1750 PSI	Reactor, 1/8" I.D. Tube
Temperature 650°C	3 Ft. Heated Section
Catalyst Concentration, 0.06 Weight Metal/Weight Coal (MAF)	

Just which form of zinc is catalytically active is not known. We do know that the chloride reacts with aldehydes, ketones and ether oxygen configurations to form complexes. We find that when zinc chloride is impregnated onto coal surfaces, all is not recovered by water extraction. After the coal has been heated even less of the zinc can be extracted by water alone. Table 3 shows the forms of zinc that we have identified in the char product where almost all the zinc is found after reaction. The residual zinc chloride is water soluble but zinc metal, basic zinc chloride and zinc oxide are insoluble in water and require an acid for solution. The basic zinc chloride is formed by reaction with water at elevated temperatures. We have found the zinc metal in char samples and have found zinc oxide in samples subjected to microwave ashing to remove the carbonaceous material. We have not verified the presence of zinc sulfide, but feel that it may be the form of zinc least soluble in hydrochloric acid and therefore a suspect as to the form in which the zinc is most difficultly recoverable.

Table III. Compounds of Zinc in Char

Coal	Char	Solubility
	$ZnCl_2$	H_2O
	Zn	HCl
$ZnCl_2$	$ZnCl_2 \cdot 4Zn(OH)_2$*	HCl
	ZnO**	HCl
	ZnS (not verified)	Slowly soluble in HCl

* Found in H_2O insoluble portion of heated H_2O solution of $ZnCl_2$

** Found in ash from low temperature ashing of char to remove organic matter and carbon.

Figure 7 shows the recovery from reacted char, using hydrochloric and sulfuric acids, 10 percent in each case. The lower designation is the number of times the same sample was extracted with equal portions of fresh hot acid. About half the zinc, as measured by the intensity of the zinc K alpha x-ray fluorescence line, is readily extracted but the remainder is only slowly extracted. It could be a rather long and involved procedure to recover all the zinc by acid extraction alone.

Because of the fact that zinc sulfide is a potential form of the zinc after the reaction we have considered some methods for dissolving this product. Table 4 shows some solution reactions together with the solubility products involved. Dissolving ZnS in HCl is possible by virtue of the formation of slightly ionized H_2S and the volitilization of H2S from the solution. Dissolving ZnS in solutions of Pb^{++}, Cu^{++} or Hg^{++} ions is possible because these metal ions form sulfides even less soluble than ZnS. Mercury sulfide particularly is very insoluble.

Table IV. Some Reactions for Dissolving ZNS.

ZnS(solid) + HCl	Zn^{++} + 2Cl- + H_2S	ZnS	K_{SP} = 1.2 x 10-23 (18°C)
ZnS(solid) + Pb^{++}	Zn^{++} + PbS(solid)	PbS	K_{SP} = 3.4 x 10-28 (18°C)
ZnS(solid) + Cu^{++}	Zn^{++} + CuS(solid)	CuS	K_{SP} = 8.5 x 10-45 (18°C)
ZnS(solid) + Hg^{++}	Zn^{++} + HgS(solid)	HgS	K_{SP} = 4.0 x 10-53 (18°C)

Figure 8 shows the extraction of zinc from reacted coal char, first with hot water, then with hot concentrated hydrochloric acid and then with hot dilute solutions of Pb^{++}, Cu^{++}, and Hg^{++} ions. We notice first that the difficulty of removing zinc from the char is directly related to the amount of conversion. For high conversion less zinc is dissolved by the solvent. Longer exposure to the Hg^{++} ion would probably result in essentially complete recovery. This approach is not practical for actual recovery of zinc, but it does illustrate that the zinc is present in the char in a very insoluble form, probably as the sulfide and that some extreme method will be required to recover the catalyst. Tests have indicated that char can be recycled with fresh coal and catalyst without loss of catalytic character. These tests have further indicated that recycled char by itself can be further hydrogenated. The resulting product is higher in gas and lower in liquids than the first cycle but the percent conversion is near to that in the first case. These tests need further study and verification because the difficulty of feeding char alone makes these tests less reliable than when coal alone is fed.

References

1. Qader, S. A., Haddadin, R. A. Anderson, L. L., Hill, G. R., Hydrocarbon Processing **48**, No. 9, 147 (1969).

2. Wood, R. E., Anderson, L. L., and Hill, G. R., Quarterly of the Colorado School of Mines, Vol. **65**, No. 4, 201 (1970).

Conditions
Last Chance, Utah, Coal 40-100 mesh   Feed Rate 10-12 g/m
Pressure 1750 PSI   Reactor, 1/8" I.D. Tube
Temperature 650°C   3 Ft. Heated Section
Catalyst Concentration, 0.06 Weight Metal/Weight Coal (MAF)

Just which form of zinc is catalytically active is not known. We do know that
the chloride reacts with aldehydes, ketones and ether oxygen configurations to form
complexes. We find that when zinc chloride is impregnated onto coal surfaces, all
is not recovered by water extraction. After the coal has been heated even less of
the zinc can be extracted by water alone. Table 3 shows the forms of zinc that we
have identified in the char product where almost all the zinc is found after reaction.
The residual zinc chloride is water soluble but zinc metal, basic zinc chloride and
zinc oxide are insoluble in water and require an acid for solution. The basic
zinc chloride is formed by reaction with water at elevated temperatures. We have
found the zinc metal in char samples and have found zinc oxide in samples subjected
to microwave ashing to remove the carbonaceous material. We have not verified the
presence of zinc sulfide, but feel that it may be the form of zinc least soluble
in hydrochloric acid and therefore a suspect as to the form in which the zinc is
most difficultly recoverable.

Table III.   Compounds of Zinc in Char

Coal	Char	Solubility
	$ZnCl_2$	H_2O
	Zn	HCl
$ZnCl_2$	$ZnCl_2 \cdot 4Zn(OH)_2$*	HCl
	ZnO**	HCl
	ZnS (not verified)	Slowly soluble in HCl

 * Found in H_2O insoluble portion of heated H_2O solution of $ZnCl_2$
** Found in ash from low temperature ashing of char to remove organic matter
   and carbon.

Figure 7 shows the recovery from reacted char, using hydrochloric and sulfuric
acids, 10 percent in each case. The lower designation is the number of times the
same sample was extracted with equal portions of fresh hot acid. About half the
zinc, as measured by the intensity of the zinc K alpha x-ray fluorescence line, is
readily extracted but the remainder is only slowly extracted. It could be a rather
long and involved procedure to recover all the zinc by acid extraction alone.

Because of the fact that zinc sulfide is a potential form of the zinc after
the reaction we have considered some methods for dissolving this product. Table
4 shows some solution reactions together with the solubility products involved.
Dissolving ZnS in HCl is possible by virtue of the formation of slightly ionized
H_2S and the volitilization of H2S from the solution. Dissolving ZnS in solutions
of Pb^{++}, Cu^{++} or Hg^{++} ions is possible because these metal ions form sulfides even
less soluble than ZnS. Mercury sulfide particularly is very insoluble.

Table IV.   Some Reactions for Dissolving ZNS.

ZnS(solid) + HCl	Zn^{++} + 2Cl- + H_2S	ZnS	K_{sp} = 1.2 x 10-23 (18°C)
ZnS(solid) + Pb^{++}	Zn^{++} + PbS(solid)	PbS	K_{sp} = 3.4 x 10-28 (18°C)
ZnS(solid) + Cu^{++}	Zn^{++} + CuS(solid)	CuS	K_{sp} = 8.5 x 10-45 (18°C)
ZnS(solid) + Hg^{++}	Zn^{++} + HgS(solid)	HgS	K_{sp} = 4.0 x 10-53 (18°C)

Figure 8 shows the extraction of zinc from reacted coal char, first with hot water, then with hot concentrated hydrochloric acid and then with hot dilute solutions of Pb^{++}, Cu^{++}, and Hg^{++} ions. We notice first that the difficulty of removing zinc from the char is directly related to the amount of conversion. For high conversion less zinc is dissolved by the solvent. Longer exposure to the Hg^{++} ion would probably result in essentially complete recovery. This approach is not practical for actual recovery of zinc, but it does illustrate that the zinc is present in the char in a very insoluble form, probably as the sulfide and that some extreme method will be required to recover the catalyst. Tests have indicated that char can be recycled with fresh coal and catalyst without loss of catalytic character. These tests have further indicated that recycled char by itself can be further hydrogenated. The resulting product is higher in gas and lower in liquids than the first cycle but the percent conversion is near to that in the first case. These tests need further study and verification because the difficulty of feeding char alone makes these tests less reliable than when coal alone is fed.

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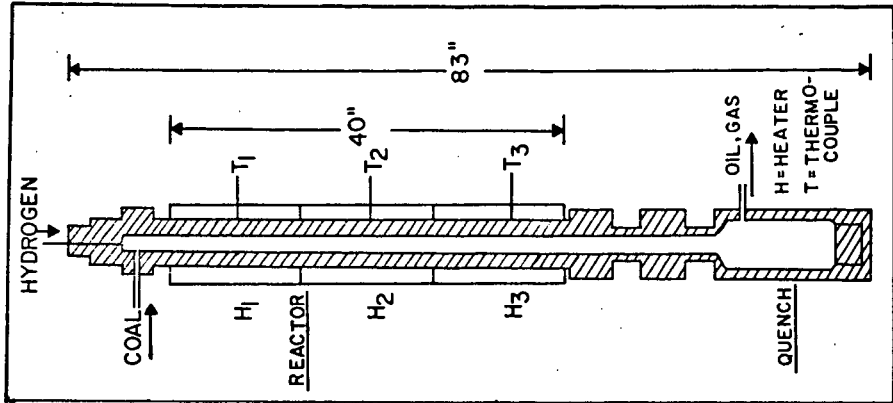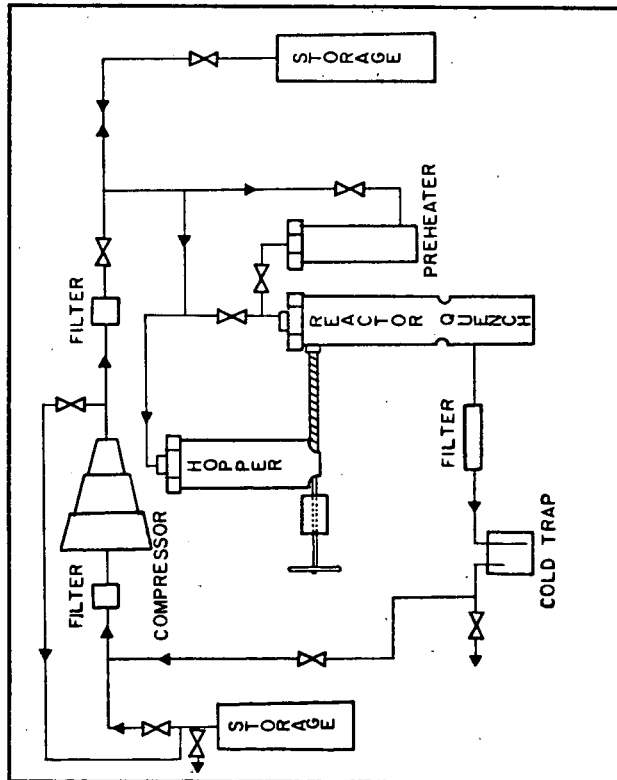
FIGURE 2. O.C.R. REACTOR AND QUENCH TANK.

FIGURE 1. SCHEMATIC DIAGRAM OF O.C.R. FREE-FALL COAL HYDROGENATION UNIT.
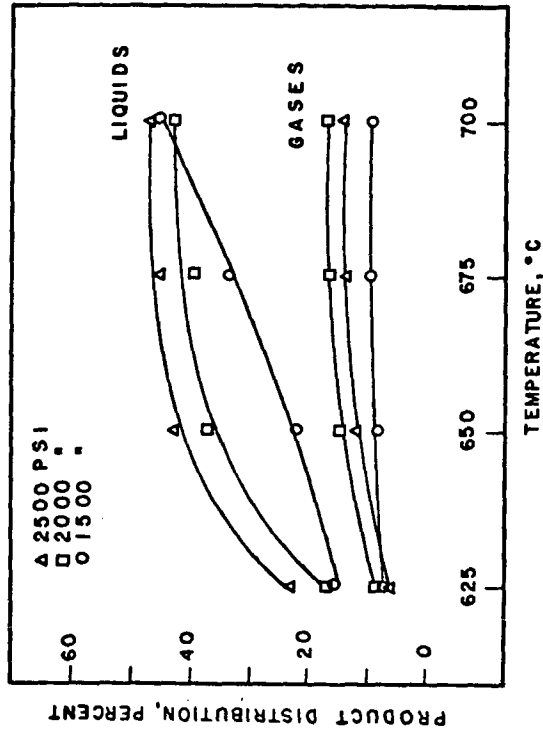
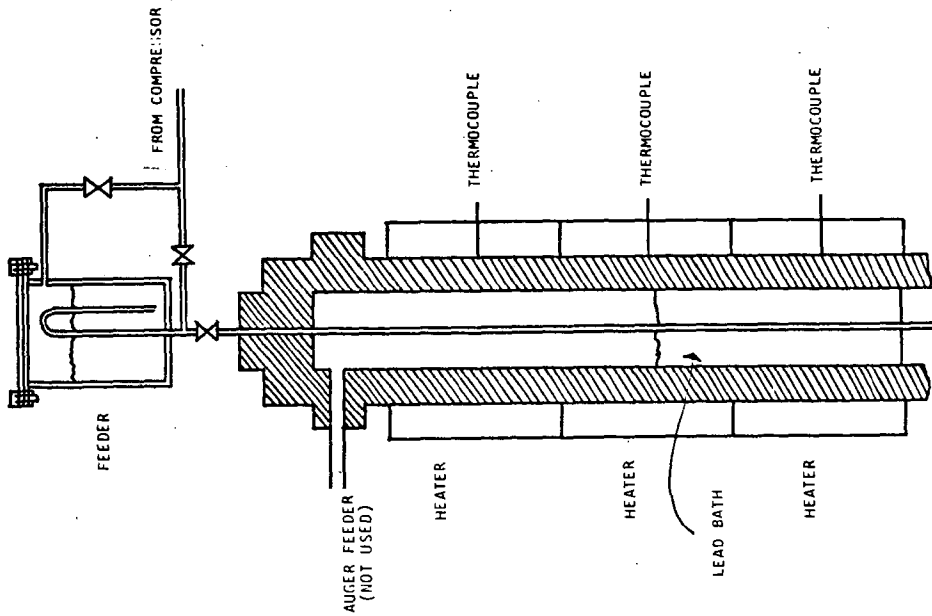FIGURE 4. PRODUCT DISTRIBUTION FOR A REACTIVE (ORANGEVILLE, UTAH) COAL.

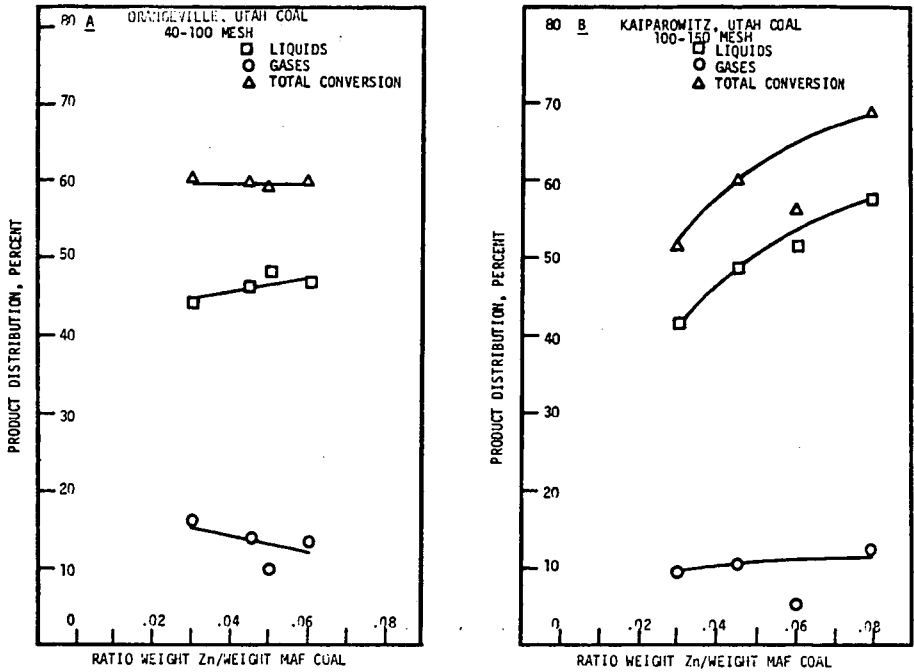FIGURE 3. FLUIDIZED FEEDER WITH 1/8 INCH REACTOR.

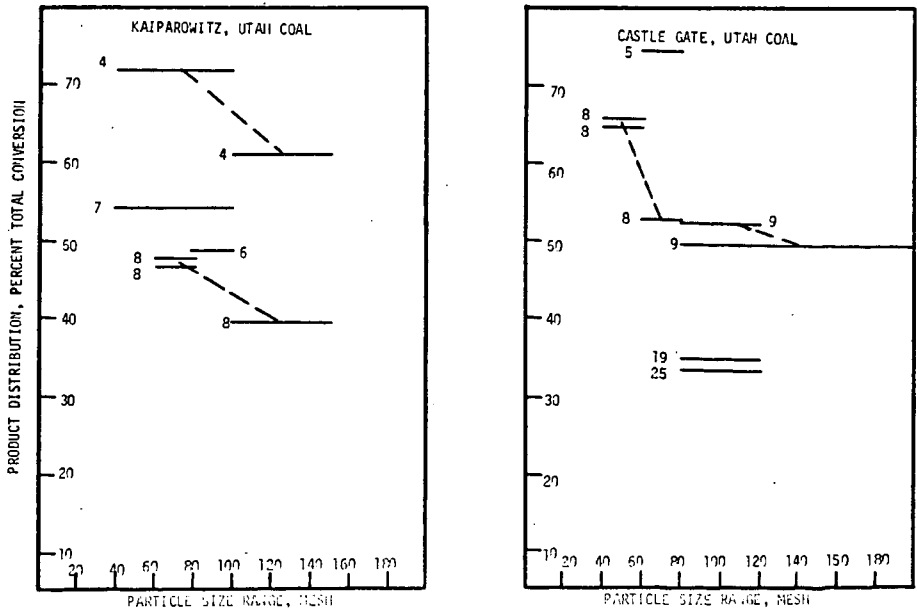FIGURE 5. EFFECT OF CATALYST CONCENTRATION ON COAL CONVERSION

FIGURE 6. EFFECT OF PARTICLE SIZE AND FEED RATE ON CONVERSION OF COAL
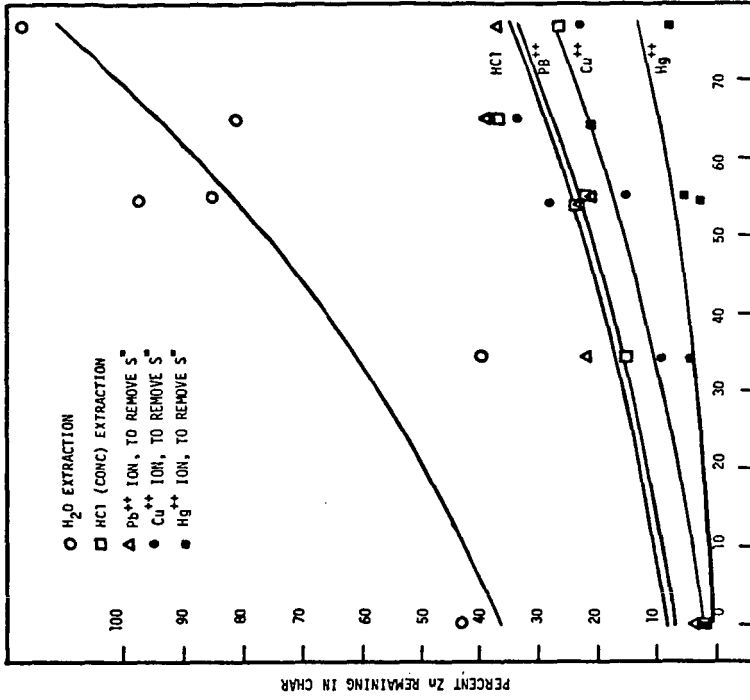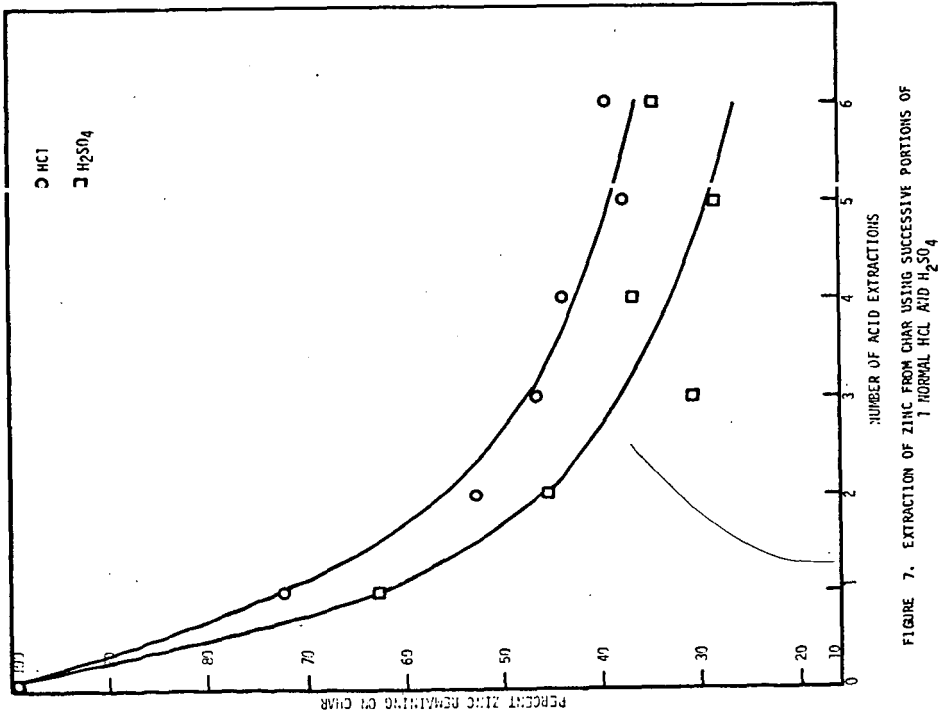
FIGURE 8. EXTRACTION OF ZINC FROM CHAR FOLLOWING COAL HYDROGENATION

FIGURE 7. EXTRACTION OF ZINC FROM CHAR USING SUCCESSIVE PORTIONS OF 1 NORMAL HCL AND H_2SO_4

CONVERSION OF BOVINE MANURE TO OIL

Y. C. Fu, S. J. Metlin, E. G. Illig, and I. Wender

Pittsburgh Energy Research Center, U. S. Department of the Interior,
Bureau of Mines, 4800 Forbes Avenue, Pittsburgh, Pennsylvania 15213

INTRODUCTION

Agriculture is the biggest source of wastes in the United States. Livestock on American farms produce over 2 billion tons of manure each year (approximately 400 million tons of organic matter), and these animal wastes are becoming a pollution, odor, and health problem. Efforts are being made by the Bureau of Mines to develop better and more efficient disposal methods using pyrolysis (1) and combustion (2) techniques. Animal waste is also a vast, untapped potential energy source if it can be converted to fuel.

Organic solid wastes, including urban refuse, agricultural wastes, sewage sludge, and bovine manure can be converted to oil by reaction with carbon monoxide and water at temperatures of 350° to 400°C and pressures near 4000 psig (3,4). The present work deals more extensively with the conversion of bovine manure to oil, and investigates effects of using synthesis gas (H_2:CO = 0.9:1) or hydrogen in place of carbon monoxide, and of adding catalyst and vehicle. It shows that synthesis gas can be used in place of carbon monoxide to convert manure to oil in reasonably good yield. Significant process improvements, such as low operating pressure and less energy requirement for heating, are achieved by the use of water:manure ratio as low as 0.25:1 with a suitable high boiling vehicle.

EXPERIMENTAL

The conversion of manure to oil with carbon monoxide and water was studied in a 1-liter magnetically-stirred stainless steel autoclave. Bovine manure from three sources was used. In the temperature range of 300° to 400°C, the operating pressure ranged from 2400 to 5300 psi. Most of these experiments were carried out for 0.5 to 1 hour at the reaction temperature. After the experiment, rapid internal cooling of autoclave to ambient temperature was achieved. Gaseous products were analyzed by mass spectrometry, and heavy oil products containing residue were separated from water and extracted by benzene to determine the amounts of the oil and the residue. The conversion of organic matter in manure was obtained by subtracting the weight percent of residue (excluding ash) from 100. Data on oil yield and carbon monoxide consumption were given on the basis of moisture-ash-free manure.

No catalyst was added for the conversion of manure with carbon monoxide and water. But in some runs using hydrogen or synthesis gas (H_2:CO = 0.9:1) in place of carbon monoxide, hydrogenation catalysts were used in an attempt to improve oil yield and hydrogen utilization.

RESULTS AND DISCUSSION

As shown in Table 1, both conversion and oil yield increased with temperature in the 300° to 380°C range, and the organic matter in bovine manure was almost completely converted by the reaction with carbon monoxide and water at 380° and 400°C. The variation in carbon monoxide consumption correlates well with the oil

yield as shown in Figures 1 and 2 and is in the range of 0.7 to 0.8 gram/gram manure at the best conversion. Figure 2 also shows that there is no increase in oil production or carbon monoxide consumption after 15 minutes reaction time at $380^{\circ}C$. The unconverted residue was inorganic, mostly silica. The extent of gas evolution owing to the thermal decomposition of manure appeared to be minor based on carbon balance in the gas phase, but the net weight increase in the gas phase amounted to as much as 37 weight percent on the organic manure basis at $400^{\circ}C$, because of the oxygen removal from manure to form carbon dioxide and concurrent water-gas shift reaction to form carbon dioxide and hydrogen. In addition, substantial amounts of water-soluble compounds were present in the yellowish water layer. On standing in the air, the solution darkened and a precipitate formed. The aqueous solution was evaporated to dryness and the residue was analyzed by infrared spectroscopy. Strong bands in the 1600 cm^{-1} region (corresponding to formates and acetates) were observed.

TABLE 1. <u>Effect of temperature on conversion of bovine manure (maf basis)</u>

(manure[a] as received 40 g, water 160 g, 600 psi initial CO pressure, 1 hour reaction time)

Temp, $^{\circ}C$	Operating pressure, psi	Conversion, percent	Oil yield, percent	Weight increase in gas phase, percent of manure	CO consumption, g/g manure
300	2440	79	14	20	0.13
350	3650	95	30	25	0.41
380	4780	99	38	35	0.70
400[b]	5300	99	38	37	0.81

[a] For analysis of manure, see Table 2.
[b] Reaction time is 30 minutes.

The analysis of manure and its products in Table 2 shows that treatment of manure with carbon monoxide and water results more in oxygen removal than in hydrogen addition. The hydrogenation effect is not apparent from the product analysis, because the starting manure probably contains many hydroxyl groups which contribute to the hydrogen content. Elemental analysis of the oil product did not vary significantly between 300° and $400^{\circ}C$. The oil product obtained at $380^{\circ}C$ has a softening point below room temperature, a kinematic viscosity in the range of 520 to 580 centistokes at 60° C, and a heating value of 16,240 Btu per pound.

TABLE 2. <u>Analysis of bovine manure and oil products, percent</u>

	Manure[a]		Oil			
	As used[b]	maf basis	$400^{\circ}C$	$380^{\circ}C$	350° C	$300^{\circ}C$
C	41.2	52.0	79.8	80.4	79.5	77.4
H	5.7	6.7	9.1	9.4	9.5	9.8
N	2.3	2.9	2.7	3.0	3.1	2.9
S	0.3	0.3	0.20	0.26	0.24	0.27
O (by diff.)	33.3	38.1	8.2	7.1	7.7	9.6
Ash	17.2	--	--	--	--	--
H/C atomic ratio		1.55	1.37	1.40	1.43	1.52

[a] Cow manure, Midwest Research Institute, Kansas City, Missouri.
[b] Moisture = 3.6 percent.

Use of hydrogen in place of carbon monoxide decreased the conversion and oil yield (Table 3). Synthesis gas (H_2:CO = 0.9:1) gave almost complete conversion but slightly lower oil yield than pure carbon monoxide, at a considerable reduction in the consumption of carbon monoxide. Some hydrogenation catalysts were used in an attempt to promote the utilization of hydrogen present in the gas phase. Cobalt molybdate appeared to have a favorable effect on the conversion of manure with hydrogen, but not when synthesis gas was used. When sodium carbonate was used with synthesis gas, a significant improvement in oil yield was obtained. An increase in autoclave pressure was also observed, indicating a greater degree of water-gas shift reaction as a result of the addition of sodium carbonate.

At a temperature of 450°C, significant improvements in oil product quality were observed in that the carbon content was increased, oxygen content was decreased, and viscosity was reduced (Table 4). The change in the oil product properties is accompanied by some decrease in the oil yield, mainly because the oxygen-containing groups are further reduced and/or removed. At this temperature, cobalt molybdate catalyst appears to have a beneficial effect in reducing the viscosity of the oil product. Hydrogen gave a more fluid product than synthesis gas.

The organic matter of manure contains about 40 percent oxygen which during the conversion process will be removed in the form of carbon dioxide, water, and water-soluble compounds. Based on our experience, we speculate that at best an oil yield of about 50 percent can be realized. Above experiments using water and carbon monoxide or synthesis gas have shown that the oil yield from manure is reasonable.

Water functions both as the reactant and vehicle. Water is the least expensive vehicle, but it has two economic disadvantages in a commercial process (1) operating pressure can become too high because of the high vapor pressure of steam at the reaction temperature, and (2) a large amount of energy is required to heat and vaporize water. Some experiments were carried out using only small amounts of water in the presence of a low-vapor pressure and less energy-requiring vehicle. An alkylnaphthalene-based oil (boiling above 235°C) was used as the vehicle. The results in Table 5 indicate that the water:manure ratio can be reduced to as low as 0.25:1 while giving 83 percent oil product yield based on feed of maf manure plus vehicle. As discussed earlier, if one assumes that only 50 percent of organic matter in manure can be converted to oil, the maximum obtainable oil product yield based on maf manure plus vehicle would be 87.5 percent. If we assume a 98 percent recovery for the vehicle as we found in a blank run, the above 83 percent yield based on feed would be equivalent to 38 percent oil yield based on maf manure. The operating pressure is also reduced significantly as the water:manure ratio is decreased. This reduction in pressure and use of a vehicle oil (generated in the process) significantly decrease the high capital investment and operating cost of the manure to oil process.

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TABLE 3. Effects of hydrogen or synthesis gas[a] on conversion

(160 g water, 40 g manure as received, 2 g catalyst, 600 psi initial pressure, 1 hour at 380°C)

Gas	Catalyst	Operating pressure, psi	Conversion, percent	Oil yield, percent	Weight increase in gas phase, percent of manure	CO consumption, g/g manure
H_2	--	4500	83	21	18	--
H_2	$SnCl_2$	4360	81	22	19	--
H_2	CoMo	4540	90	27	22	--
H_2 + CO	--	4740	99	34	30	0.41
H_2 + CO	CoMo	4680	99	33	28	0.40
H_2 + CO	Na_2CO_3	4790	99	38	35	0.48
H_2 + CO	CoMo + Na_2CO_3	4770	99	38	35	0.47

[a] H_2:CO = 0.9:1.

TABLE 4. Conversion of steer manure[a] at 450°C (maf basis)

(reaction time ≃ 0.5 hour)

Gas	H_2	$H_2 + CO$[b]	$H_2 + CO$[b]
Water:manure	0:1	1:1	1:1
Catalyst[c]	CoMo	CoMo	--
Operating pressure, psi	3700	4150	4200
Conversion, percent	99	99	99
Oil yield, percent	15	22	21
Oil analysis,			
C	85.3	82.6	81.3
H	8.8	8.4	8.5
N	3.6	6.0	6.9
S	0.33	0.33	0.24
O (by diff.)	1.97	2.67	3.06
H/C atomic ratio	1.24	1.22	1.25
Kinematic viscosity of oil at 60°C, centistoke	10	133	252

[a] Texas steer manure; analysis, percent: C = 25.5, H = 4.0, N = 2.6, S = 0.4, O = 22.8, ash = 44.7, moisture = 5.7.

[b] $H_2:CO = 0.9:1$.

[c] 3.3 parts per hundred parts manure.

TABLE 5. Effect of vehicle

(1000 psi initial synthesis gas[a] pressure, 380° C)

Water:manure:vehicle[b][c]	1:1:2.5	0.5:1:2.5	0:25:1:2.5	0.25:1:2.5
Catalyst	--	--	Na_2CO_3	--
Operating pressure, psi	3400	3100	2800	3300[d]
Time, hr	0.5	0.5	1	0.5
Conversion, percent	94	91	95	89
Oil product yield, percent feed[e]	84	83	83	82

[a] $H_2:CO = 0.9:1$.

[b] Beef cattle manure, Beltsville, Md.; analysis, percent: C = 44.7, H = 6.4, N = 3.0, S = 0.37, O = 37.2, ash = 8.3, moisture = 5.9.

[c] An alkylnaphthalene-based oil, Sunoco.

[d] 1260 psi initial pressure.

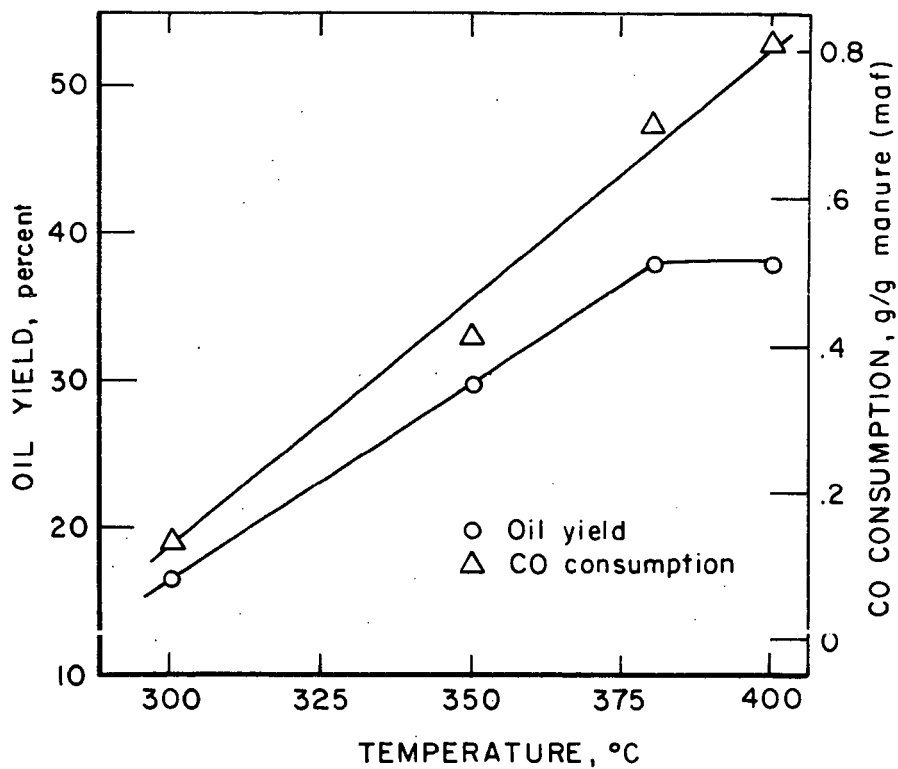[e] Based on feed of maf manure plus vehicle.

Figure 1- Effect of temperature on oil yield and CO consumption
at 1 hour reaction time.
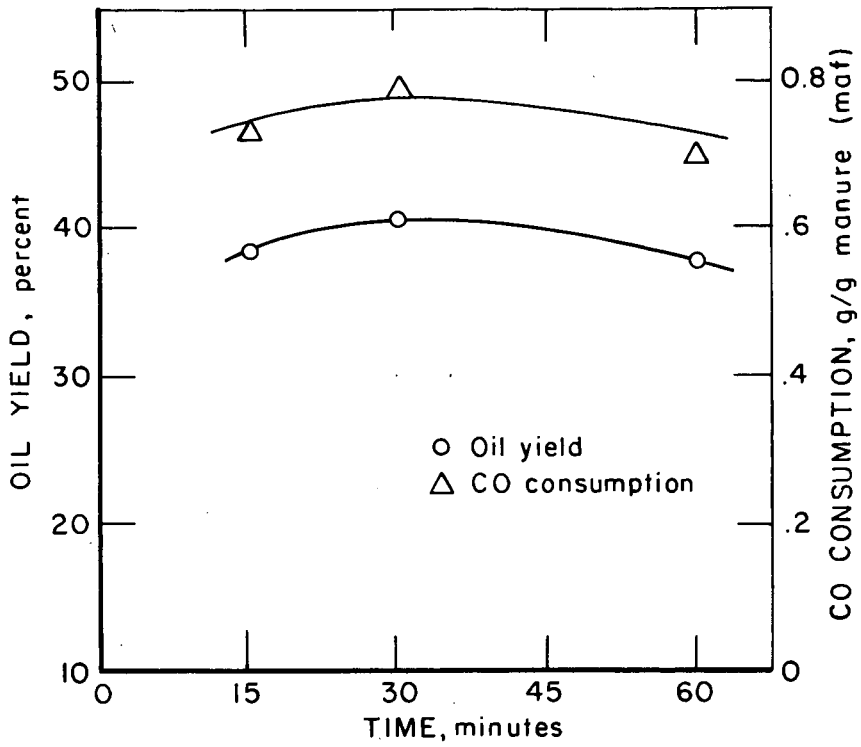
4-24-72   L- 12857

Figure 2 — Effect of reaction time on oil yield
and CO consumption at 380°C.
4-24-72   L-12858

PREPARATION OF ASH-FREE, PYRITE-FREE COAL BY MILD CHEMICAL TREATMENT

Leslie Reggel, Raphael Raymond, Irving Wender, and Bernard D. Blaustein

Pittsburgh Energy Research Center, U. S. Department of the Interior,
Bureau of Mines, 4800 Forbes Avenue, Pittsburgh, Pennsylvania 15213

The major fraction of the electricity generated in the United States is produced
by coal-fired power plants, and the demand for electricity is increasing rapidly.
Low-sulfur coals meeting air pollution specifications for utility use are in
short supply in the eastern part of the country. Low-sulfur fuel oils which are
also used to generate electricity are limited in domestic supply, are costly,
and usually must be obtained from foreign sources. Removal of sulfur from coal,
either before, during, or after combustion (i.e., removal of sulfur oxides from
stack gas), to meet air quality standards, is therefore one of the most pressing
needs in the related fields of energy and clean environment. Numerous processes
for sulfur removal are being actively investigated by many organizations, in-
cluding the Bureau of Mines of the U. S. Department of the Interior.

Sulfur in coal occurs as sulfate; as pyrite, FeS_2; and as organic sulfur which is
part of the coal structure. The sulfate is usually low. In experiments being
carried out at the Pittsburgh Energy Research Center of the Bureau of Mines,
almost all of the pyritic sulfur has been removed from some coals by treatment
with aqueous alkali. For example, 30 g of -200 mesh Illinois No. 6 high volatile
B bituminous coal is treated with a solution of 24 g of sodium hydroxide in 240
ml of water for 2 hr at 225° in a stirred autoclave, followed by acidification of
the coal-aqueous alkali slurry with carbon dioxide. (The solution of sodium
hydroxide used is referred to as "10% aqueous NaOH" in the tables.) In this treat-
ment, the pyritic sulfur is removed, but the organic sulfur in the coal is not
attacked by this procedure; for some coals, removal of pyritic sulfur would give
a product that meets present specifications for sulfur content for use in power
plants. The solid product obtained by this experimental procedure has a somewhat
higher ash content than does the original coal. However, if the sodium hydroxide
treatment is followed by acidification with dilute hydrochloric acid (instead of
carbon dioxide), most of the mineral matter originally present is removed from the
coal. The starting Illinois No. 6 coal contains 9.8% ash and 1.1% pyritic sulfur;
the product contains 0.7% ash and 0.1% pyritic sulfur. The yield of coal is 91.5%
(maf basis).

Table 1 gives the results of various experiments with Illinois No. 6 coal. The
organic sulfur is reported on a moisture- and ash-free basis, since removal of
ash and/or pyrite will concentrate the organic sulfur and make it seem to increase.
It is noted that in some runs the organic sulfur does increase, even on an maf
basis, and even allowing for the fact that the analysis is by difference and
subject to an inherently large (but uncertain) error.[1]

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[1] Organic sulfur in coal cannot be determined by any direct method. The standard
procedure is to determine total sulfur, sulfate sulfur, and pyritic sulfur. The
sulfate sulfur and the pyritic sulfur are subtracted from the total sulfur and
the remainder is assumed to be organic sulfur. In an indirect method such as
this, the probable error of the organic sulfur must be larger than the largest
probable error of the three values from which it is derived.

TABLE 1. Illinois No. 6 (River King) hvbb coal: effect of 10% aqueous NaOH
for 2 hr at 225°, followed by various acid workups, on ash and
sulfur content (analyses on dry basis)

Run 11R-	Treatment	Workup	Ash	S total	S sulfate	S pyritic	S organic (diff., maf)
37	None	-	9.8	3.26	0.21	1.08	2.19
37A	NaOH	CO_2	12.4	2.05	0.11	0.13	2.06
83A	NaOH	CO_2	12.2	2.25	0.18	0.16	2.17
93	None	-	9.82	3.27	0.31	1.05	2.12
96	$Ca(OH)_2$	HCl	8.16	3.04	0.04	1.04	2.14
97	NaOH	HCl	0.67	2.54	0.01	0.11	2.44
103	None	-	9.77	3.30	0.33	0.92	2.28
103A	NaOH	HCl	0.84	2.58	0.00	0.09	2.51
110	None	-	9.85	3.28	0.42	0.93	2.14
110A	H_2O	CO_2	9.46	2.77	0.01	0.98	1.96
111A	H_2O	HCl	8.76	2.85	0.01	1.04	1.98
112	None	-	9.84	3.20	0.42	0.96	2.01
112A	NaOH	SO_2	0.72	2.40	0.23	0.19	1.99
113A	NaOH	H_2SO_4	0.52	2.75	0.24	0.19	2.33
133	None	-	12.58	3.69	0.09	1.39	2.53
133A	NaOH	Aspirate; H_2SO_4 slowly	0.85	2.99	0.17	0.12	2.73
134	NaOH	Aspirate; H_2SO_4 slowly	0.59	2.96	0.20	0.18	2.59
135	NaOH	Aspirate; H_2SO_4 dropwise	0.91	2.82	0.09	0.16	2.59
136	30% NaOH	Aspirate; H_2SO_4 dropwise	0.87	2.84	0.07	0.06	2.73

The erratic increase in organic sulfur mentioned above is puzzling. It is possible
that elemental sulfur is precipitated either at some stage of the reaction, or
during the workup of the product; free sulfur would be reported as organic sulfur
in the standard analytical procedure for sulfur forms. (In a modification of the
standard procedure, where the organic sulfur is determined by taking the residue
from the pyrite determination and analyzing for sulfur, free sulfur would also be
reported as organic sulfur.) An attempt was made to settle this question by
extraction (Soxhlet) of a coal sample with ethanol, and analysis of the extract
for sulfur by ultraviolet spectrometry; no sulfur was found. It is also possible
that at some point in the procedure, free sulfur or polysulfide ion is formed and
attacks the coal, giving an actual increase in organic sulfur.

One possible method of preventing an increase in organic sulfur would be to remove
the sulfide-containing alkali solution from contact with the coal before any work-
up is done. (This assumes that the troublesome sulfur material is in solution and
is not already adsorbed on the coal surface.) This technique, using a filter
stick, has been used on those runs which are marked (in the tables) as "aspirate."
This aspiration procedure removes about 70-90% of the alkaline solution. Obviously,
in any commercial procedure, filtration, centrifugation, or some other process would
be used in order to recover caustic solution for re-use, to minimize the amount of
acid needed, and also to recover minerals and sulfur dissolved in the alkali.

There is some evidence that the aspiration of the caustic results in less of an increase of organic sulfur (table 1, run 113A compared with runs 133A, 134, 135). There is also evidence that aspiration results in better removal of ash and pyrite (table 2, runs 119A and 121A).

TABLE 2. Elliot mine mvb coal: effect of 10% aqueous NaOH for 2 hr at 225°, followed by various workups, on ash and sulfur content (analyses on dry basis)

Run 11R-	Treatment	Workup	Ash	S total	S sulfate	S pyritic	S organic (diff., maf)
99	None	-	18.15	4.31	0.20	3.25	1.05
99A	NaOH	CO_2	22.84	2.27	0.19	0.19	2.44
104	None	-	18.21	4.31	0.26	3.29	0.93
104A	NaOH	HCl	5.11	3.61	0.01	1.94	1.75
114	None	-	19.86	5.21	0.32	3.74	1.44
114A	NaOH	HCl (special)	4.06	4.06	0.01	2.39	1.73
115A	NaOH, 7 hr	HCl	5.84	3.88	0.10	2.08	1.81
116A	30% NaOH	HCl	3.03	3.16	0.03	0.75	2.45
117A	NaOH, 325°	HCl	8.43	2.77	0.04	0.48	2.46
119-1	None	-	19.68	5.23	0.35	3.85	1.28
119A	NaOH	H_2SO_4	7.26	5.21	0.06	3.35	1.94
120A	NaOH	H_2SO_4 (special)	4.56	4.38	0.14	2.46	1.85
121A	NaOH	Aspirate; H_2SO_4	6.06	3.79	0.07	2.54	1.25
122A	NaOH	Aspirate; H_2SO_4 (special)	4.07	3.52	0.19	1.97	1.41
126A	Double volume 10% NaOH	Aspirate; H_2SO_4	5.24	3.49	0.13	1.86	1.58

The use of sulfur dioxide for the acidification step (table 1, run 112A) gave good results, suggesting that it might be possible to use sulfur oxides from stack gas for the process. It is noteworthy that sulfur dioxide is a strong enough acid to cause the deashing reaction to take place, but carbon dioxide is not effective for deashing.

The chemistry of the dissolution of pyrite in aqueous alkali is not known, but something can be suggested with regard to the deashing reaction. The following mechanistic scheme is based upon the reactions which take place in purification of alumina from bauxite ore. When a coal is treated with alkali, the clay minerals probably dissolve and then precipitate as a stable insoluble sodium aluminum silicate of composition $3Na_2O \cdot 3Al_2O_3 \cdot 5SiO_2$. This is not soluble in alkali but is soluble in strong acid. Thus, after acidification, the silica, alumina, and some other mineral matter of the coal should be found mostly in the acid fraction, with only a small amount in the alkaline fraction. Preliminary analytical data confirm this hypothesis.

In table 3, runs 124A and 125A give the results of alkali deashing-depyriting in the presence of hydrogen. The coal itself had a somewhat different behavior during workup; it tended to float during centrifugation. There was no uptake of gas and the results were similar to runs made under similar conditions in the absence of hydrogen (table 2). Further experiments are desirable, since the runs using

hydrogen gave relatively low ash and pyrite values. Run 128A was done in the presence of 1700 psi initial pressure of synthesis gas (0.9 H_2:1 CO). At the end of the reaction, the aqueous layer had a pH of about 5. It is obvious that the carbon monoxide reacted with the sodium hydroxide to give sodium formate. Analysis of the gases showed that 0.58 mole of carbon monoxide was used up, corresponding well to the 0.60 mole of sodium hydroxide initially present; the calculation also indicated the formation of 0.15 mole of hydrogen. Removal of pyrite is good (82% removed) but removal of ash is poor (only 49% removed). This suggests two possibilities. With neutralization of the sodium hydroxide via the formation of sodium formate, ash removal must be a relatively slow reaction or may require a fairly high alkali concentration, so that rate of mineral conversion becomes very slow after a short time. On the other hand, rate of pyrite reaction with sodium hydroxide must be fairly rapid, or else continues even in weak alkali, so that the final pyrite removal is still good. Another possibility, but a rather unlikely one, is that some of the pyrite is dissolved not by the alkali but by the formic acid. Pyrite is not soluble in dilute hydrochloric acid, but formic acid is a reducing agent, which may have some effect upon the pyrite.

TABLE 3. Effect of various gases in the presence of 10% aqueous NaOH, followed by acid workup, on the ash and sulfur of coal (dry basis)

Run 11R-	Coal	Treatment	Workup	Ash	S total	S sulfate	S pyritic	S organic (diff., maf)
119-1	Elliot	None	-	19.68	5.23	0.35	3.85	1.28
124A	Elliot	H_2, NaOH 250°	H_2SO_4	3.72	2.48	0.08	0.64	1.84
125A	Elliot	H_2, NaOH, 250°	H_2SO_4	3.39	2.26	0.02	0.29	2.02
128A	Elliot	H_2 + CO, NaOH, 250°	Aspirate; H_2SO_4	10.03	2.41	0.06	0.69	1.85
133	River King	None	-	12.58	3.69	0.09	1.39	2.53
137	River King	Air, NaOH, 225°, 1 hr	Aspirate; H_2SO_4	14.27	2.10	0.05	0.21	2.16

Run 137 in table 3 shows the effect of air (760 psi at room temperature) upon the reaction of River King coal with sodium hydroxide. There was an uptake of oxygen. The aspirate had a pH of 5.5-6.0 (probably bicarbonate with dissolved carbon dioxide) and the oxygen content of the coal increased from 9.66 to 10.37%. Probably the oxygen and alkali oxidized some of the coal to "humic acids," using up the alkali in this reaction. The ash content increased, the pyritic sulfur decreased, but the sulfate was almost unchanged. The results suggest that the pyrite was rapidly attacked and converted to water-soluble sulfate; this is substantiated by the observation that during the acidification of the treated coal, there was no odor of either hydrogen sulfide or sulfur dioxide, though there was copious evolution of an odorless gas, presumably carbon dioxide. The organic sulfur (moisture- and ash-free basis) decreased from 2.53 to 2.16%. Since the increase in oxygen content of the coal would decrease the organic sulfur by dilution, these figures can be put on a moisture-, ash-, and oxygen-free basis; the change is then from 2.84 to 2.46% organic sulfur. This decrease in organic sulfur is small and probably subject to a fairly large analytical error; however, it does seem to be significant, in view of the fact that the organic sulfur tends to increase slightly in most other experiments.

One run (table 1, run 96) was made using aqueous calcium hydroxide, which would be a cheaper source of alkali than sodium hydroxide. The pyritic sulfur was not attacked; possibly this is because of the very limited solubility of calcium hydroxide, resulting in a very low concentration of hydroxide ion in solution.

Treatment of the coal with water at 225° (conditions used for the alkali treatment) did not have any effect; thus, there is no doubt that the deashing requires alkali and is not simply a result of a hydrothermal water treatment. This was shown to be true for both carbon dioxide workup and hydrochloric acid workup (runs 110A and 111A, table 1).

No further discussion of the results given in table 2 (Elliot mine mvb coal) and in table 4 (Indiana No. 5 hvbb coal) will be given here, except to point out that Indiana No. 5, like Illinois No. 6, has been converted to a low-ash, low-pyrite material.

TABLE 4. Indiana No. 5 hvbb coal: effect of 10% aqueous NaOH for 2 hr at 225°, followed by various acid workups, on ash and sulfur content (analyses on dry basis)

Run 11R-	Treatment	Workup	Ash	S total	S sulfate	S pyritic	S organic (diff., maf)
108	None	-	9.55	3.47	0.35	1.02	2.32
108A	NaOH	HCl	0.48	2.63	0.02	0.06	2.56
109A	NaOH	CO_2	10.57	2.35	0.16	0.13	2.31
141	None	-	9.42	3.46	0.50	0.94	2.23
141A	NaOH	Aspirate; H_2SO_4 with heating and stirring	0.72	2.56	0.20	0.15	2.23

The depyriting-deashing procedure usually increased the heating values of the coals somewhat, as would be expected. The free swelling index usually changed only slightly.

An ash-free, pyrite-free coal would have several important potential applications, which would depend on its cost and specific characteristics. Ash-free coal might simplify the process to produce synthetic high-Btu gas from coal. If it were cheap enough, ash-free, pyrite-free coal would be much preferred for combustion to generate electricity, either in conventional steam plants, gas turbines, or MHD generators. The use of ash-free, pyrite-free coal should extend the life of the catalyst used for the catalytic hydrodesulfurization of coal. An ash-free feed should simplify the process of converting coal to liquid fuels with the conventional coal hydrogenation catalysts, by eliminating the separation of oil from solid residues. Ash-free coal should also find uses as materials for the preparation of electrodes and other specialty carbon products.

Further studies of the many variables in this deashing-depyriting reaction are in progress, to develop technical and economic data required so that the applicability of the process for supplying low-sulfur fuel can be fully evaluated.

THE GAS SUPPLIES OF THE UNITED STATES--PRESENT AND FUTURE

Gordon K. Zareski, Bureau of Natural Gas

Federal Power Commission, Washington, D.C. 1/

INTRODUCTION

The growth of natural gas service in the United States between 1945 and 1970 must rank as one of the great success stories of American business and technology. During this period the number of miles of utility gas mains carrying natural gas increased from 218,000 miles to 906,925 miles, and a $17 billion high-pressure gas transmission pipeline network was extended into all of the lower 48 states. Natural gas consumption increased at an annual average rate of about 6.5 percent and moved from a position where it supplied 13 percent of the Nation's total energy consumption in 1945 to the point where it provided about 33 percent of the total energy consumed in 1970.

The Nation's gas reserves are distributed among 25,000-30,000 gas fields (shaded areas of Figure 1) which in many instances are geographically remote from the gas consuming areas. The pipeline system which connects the consuming areas with their respective areas of supply can, in a general way, be characterized by a number of national "pipeline corridors." For instance the interstate gas consumed in the New England, Great Lakes, Appalachian, and Southeastern regions (proportional to the width of the arrows in Figure 1) originates chiefly in the South Louisiana, Texas Gulf Coast, and Hugoton-Anadarko (Oklahoma Panhandle region) gas supply areas. In addition to these domestic supplies, the United States is also a net importer of gas from Canada and Mexico. Although net imports during 1970 amounted to only about 3.5 percent of national consumption, imports are an important contribution to the gas supply of some areas.

The requirements for gas are expected to increase significantly during the 1971-1990 period, not only because of the growth in total energy requirements but because of the clean nature of this fuel and its premium value from a pollution control standpoint. Unfortunately the deliverable supply of natural gas, which presents the fewest pollution problems of all the Nation's present primary energy sources, will be inadequate to meet all of the demand for it.

1/ The views expressed herein are those of the author and do not necessarily reflect the views of the Federal Power Commission or of individual Commissioners.

The American gas consumer has only recently begun to be affected by the developing imbalance between the supply of this environmentally superior fuel and the burgeoning demand for it. The emerging shortage of gas is evidenced by major pipeline companies and distributors in many parts of the country being forced to curtail service to some existing customers and to refuse requests for additional gas service from many new customers and from present large industrial customers. Present and projected trends in the supply and demand for gas in the United States indicate that the national supply deficit which has recently developed will continue throughout the 1972-1990 period.

DEMAND

Until recently gas requirements (demand) of the United States were equivalent to gas consumption, because gas supplies were abundantly available as new markets for gas were developed. In retrospect then, demand for gas was approximately equal to domestic net production plus net pipeline imports. Prospectively, however, under conditions of insufficient gas supply, consumption will be less than demand.

While numerous projections of the future demand for gas have been made, the most recent projection of future gas requirements developed by the Future Requirements Committee has been adapted in this analysis as the yardstick against which anticipated gas supply will be measured. On this basis the annual demand for gas in the lower 48 states is projected to grow from 22.6 trillion cubic feet in 1970 to 46.4 trillion cubic feet in 1990 (Figure 2). The growth of demand to this level reflects an anticipated average annual compound growth rate of about 3.7 percent during the 1970-1990 period compared to a historical average annual compound growth rate of over six percent for the 1950-1970 period.

HISTORICAL RESERVE AND PRODUCTION TRENDS

The historical domestic supply position of the United States, as reported by the American Gas Association, is illustrated in Table I and Figure 3. These data exclude Alaskan resources because they are not presently available to the markets of the lower 48 states.

Prior to 1968 the annual net additions to reserves exceeded the annual production of gas, resulting in a surplus of gas found over the amount of gas consumed. In 1968, for the first time, production exceeded reserve additions by 7.3 trillion cubic feet. This historic reversal was followed by excesses of production over reserve additions of 12.3, 10.7, and 12.5 trillion cubic feet in 1969, 1970, and 1971, respectively. Because reserve additions in the past 4 years have been considerably below the historical

level and because production has been increasing, the year-end
inventory of proved reserves has been reduced from its historical
high of 289.3 trillion cubic feet in 1967 to a current level of
247.4 trillion cubic feet.

A distinct change in the rate of production occurred during
1971 when production increased only 0.1 trillion cubic feet.
Although this change results from many factors, including the fact
that the 1971-72 winter was unseasonably mild in many parts of the
country, it may also indicate that the Nation's peak productive
capacity is being approached. As will be discussed later, this
peak has been projected to occur beginning about 1973.

One commonly used indicator of the Nation's gas supply posture
is the reserve to production (R/P) ratio. The R/P ratio is a
measure of the remaining years of proved reserves at the current
level of production. Although the R/P ratio does not consider
many of the physical limitations which govern the rate of gas
withdrawal, it is useful as an indicator of gas supply. The R/P
ratio has declined steadily from 26.8 in 1950 to 11.3 in 1971. Con-
sidered by itself, the historical decline in the R/P ratio was not a
major source of concern because it was believed by some that, ideal-
ly, the R/P ratio would stabilize at a point sufficient to enable
the quantities of gas demanded to be met without the development of
excessive reserves. A decline below the ideal level, however, re-
sults in deliverability problems, i.e. reserves are insufficient to
deliver the peak quantities of gas needed.

The findings (reserve additions) to production (F/P) ratio is
another indicator which is sometimes useful when talking about gas
supply. While reserve additions have fluctuated about an average
value, production has been increasing, causing the F/P ratio to
decline from about 2 in the early 1950's to 0.4 in 1971, indicating
that gas reserves are now being consumed faster than they are being
renewed (Figure 4).

FUTURE DOMESTIC GAS SUPPLY

Any analysis of future domestic supply necessarily involves
an estimate of the level of future reserve additions. A recent
analysis of natural gas supply and demand relationships by the
Federal Power Commission (FPC) Staff reached several conclusions
with respect to the future annual reserve additions depicted in
Figure 5. First, an increase from the present level of annual
reserve additions to the average national finding level of the
past ten years (17 trillion cubic feet annually) is consistent
with factors such as estimates of the undiscovered potential gas
remaining and recent regulatory actions which have increased the
wellhead price of gas in several important supply areas. Second,
it is unlikely that annual reserve additions will increase to a
sustained level higher than the average of the past 10 years.

Finally, it is improbable that findings will increase immedi-
ately to the 17 trillion cubic feet level from the 1970 level of
11.1 trillion cubic feet. Accordingly, for the purpose of pro-
jection, it is assumed that annual reserve additions will increase
by approximately one trillion cubic feet per year from the 1970
level of about 11 trillion until additions reach 17 trillion
cubic feet per year in 1976. Reserve additions are subsequently
projected at 17 trillion cubic feet per year during the period
1977 through 1990.

Cumulative reserve additions under this anticipated schedule
would amount to 325 trillion cubic feet from 1971 through 1990.
This rate of reserve additions is compatible with current indepen-
dent estimates of potential gas supply by the Potential Gas Commit-
tee (PGC) and the United States Geological Survey (USGS). Under
this schedule of annual reserve additions, cumulative additions
through 1990 would represent the development of about 38 percent
and 21 percent, respectively, of gas supply in the lower 48 states
as estimated by PGC and USGS.

Average reserve additions for the five year period 1971 through
1975 would be 14 trillion cubic feet per year which was also the
average experienced during the period from 1966 through 1970.
Reserve additions for 1971 were projected by the Federal Power
Commission Staff to be about 12 trillion cubic feet (Tcf). In
1971, reported additions amounted to only 9.4 Tcf. Some reserves
resulting from drilling on acreage leased in the December, 1970
Federal lease sale in offshore South Louisiana were not included,
however, because data was insufficient to properly estimate the
amount of proved reserves.

Estimates by the FPC Staff have been made of the future
annual production levels which could be supported by these project-
ed additions to reserves. The period from 1971 through 1975 was
focused on by employing the projected national additions to reserves
in an area-by-area analysis of the major producing areas of the
country. Each area was examined by evaluating past drilling
trends, reserve finding rates and production history as well as
the potential of the area for sustained contributions to
national supply. Two things were established through this analysis:
(1) our national reserve additions schedule through 1975 was
reconciled with individual supply area considerations and (2) we
were able to approximate the national production rate which could
be anticipated by summing the area-by-area estimates of produc-
tion capability.

The dynamics of the relationship between gas supply, demand,
and production can result in changing inter-area relationships
with the passage of time. For this reason production projections
based on an area-by-area approach do not have much validity

beyond five years. Beyond that time span, estimates of the production available from a given reserve base are probably best made on a national basis.

A commonly used method of approximating the productive capacity of a body of reserves is to assume that a minimum reserve to production ratio (usually 10) is required to provide for adequate delivery rates. This rule of thumb approach does not consider the sometimes rather wide variations experienced with actual gas reservoirs. In an attempt to make an improved approximation of future long-term gas deliverability, the FPC Staff developed a method to estimate the national production capability for each year by the computerized application of a "national availability curve." This curve was synthesized from FPC Form 15 deliverability data from more than 900 individual sources of supply which comprised more than 88 percent of the interstate and 62 percent of the national reserves in 1968. This method is superior to an R/P limit approach because it is derived from deliverability data which considers actual reservoir production characteristics.

The production projection for 1971 through 1990 (Figure 6) was derived from presently proved reserves plus anticipated reserve additions as scheduled by the methods described above and was computed using the "national availability curve." Annual gas production has increased exponentially in the past. In the 1971-1990 time interval, however, it is projected to peak at about 24.8 trillion cubic feet, around 1973-1974, and thereafter decline and stabilize at a somewhat lower level in the 1980's. Because demand is projected to grow while domestic supply is projected to stabilize within the time frame considered, a gas supply shortfall will develop. This supply deficit is projected to increase annually and reach 28.6 trillion cubic feet by 1990 (Table II).

Future supply and demand will not develop exactly as depicted in the above projections because precision is not possible in such a projection. Both demand and domestic production are susceptible to considerable deviation from the levels projected. In terms of sensitivity to error, it is obvious that the projection of domestic production is very susceptible because of its dependence upon the level of future reserve additions. Even if much more optimistic levels of reserve additions (and hence productive capacity) are assumed, however, increasing demand cannot be satisfied. Figure 7 illustrates a comparison of demand and three different levels of productive capacity should annual reserve additions exceed 17 trillion cubic feet per year. Reserve additions of 20, 25, and 30 trillion cubic feet are programed for every year beginning with 1971. Even under the best of these conditions, a substantial supply gap develops in the mid-1970's and worsens over the time span considered.

SUPPLEMENTAL GAS SUPPLIES

When considered against the backdrop of a projected indigenous
supply deficiency, the importance of the future role to be played
by supplemental sources of gas is obvious. Pipeline imports of gas
from Canada and Mexico constitute the only substantive source of
supplemental gas presently available. However, significant supple-
mental supplies of gas are expected to become available from
several other sources in the future as development of the associat-
ed technologies and/or required systems proceeds. These major new
supplemental sources are liquefied natural gas imports (LNG), gas
from coal, and gas from Alaska (Table III). A positive contribution
to gas supply will also be made by reformer gas derived from liquid
hydrocarbons (SNG). However, the quantification of meaningful
long range projections with respect to this source is not practi-
cable at this time.

Pipeline Imports

During 1970 net imports of natural gas to the United States
from Canada and Mexico amounted to 794.5 billion cubic feet. Of
this amount, net imports from Mexico were only 26.7 billion cubic
feet. There appears to be little reason to expect any substantial
increase in imports from Mexico chiefly because of Mexico's
relatively small undiscovered gas potential. There are prospects
for increased overland imports of gas from Canada, however, which
depend in large measure upon the timely development of gas reserves
in excess of those required to satisfy Canada's future internal
requirements.

In April 1969 the Canadian Petroleum Association estimated the
ultimate potential raw recoverable natural gas reserves of Canada
to be 720.9 trillion cubic feet (at 14.73 psia and 60°F.). If the
total raw recoverable gas discovered through 1970 is subtracted
from this value, a remaining undiscovered potential of 634.8
trillion cubic feet of raw gas is derived. Much of this undis-
covered potential is attributed to Canada's frontier areas
comprised of Northern Canada, the Arctic Islands, the MacKenzie
Delta, Hudson Bay, and the continental shelf areas off the
Atlantic, Pacific, and Arctic coasts. An important factor rela-
tive to Canada's natural gas potential is the interrelationship
between the possible development of the potential in the MacKenzie
Delta and Arctic Islands areas and the effect that this would have
in unlocking the proven and potential gas resources of Alaska.
The successful development of Canada's MacKenzie Delta and Arctic
Islands resources would greatly enhance current proposals to
move gas from Alaska and Northern Canada to Canadian and United
States markets.

Several significant gas discoveries have already been made in the frontier areas. Because of these discoveries, a future level of annual reserve additions greater than historical rates can reasonably be used to estimate the future gas surpluses which the Canadians may be able to make available for export. Annual reserve additions in Canada's traditional supply areas averaged 4 trillion cubic feet from 1966 to 1970. On the basis of the potential of the frontier areas, however, future annual average additions may be estimated to be 6.5 trillion cubic feet. Use of this finding level in conjunction with Canada's projected requirements and scheduled exports under existing licenses would result in an increase in the annually exportable volumes of 0.8 trillion cubic feet in 1970 to 1.9 trillion cubic feet by 1990 (Table III).

Liquefied Natural Gas

Many regions of the world have extensive volumes of developed natural gas reserves but have limited internal markets. These resources in conjunction with advancing technologies in the liquefaction, handling, and transportation of liquefied natural gas (LNG) have kindled an intense interest in the delivery of liquefied natural gas volumes to the energy hungry centers of the world.

At present the Federal Power Commission has authorized only one long-term marine import of LNG into the United States. Several other proposals for the long-term import of base load LNG have been filed with the Federal Power Commission, however, and a number of other prospective projects have been widely discussed in the trade press. These filed and prospective LNG projects are an indication of the future availability of long-term LNG imports to the contiguous United States. While the estimated operational dates for these projects may be based on reasonable assumptions or on the most current expectations, other more difficult factors to evaluate such as the length of time required for the necessary governmental authorizations and the construction time necessary to build the extensive facilities required make it unlikely that actual LNG imports will precisely follow current schedules and expectations. Current analyses of these projects indicate that the import of significant LNG volumes into the United States (0.3 trillion cubic feet) can first be expected in 1975 and that these imports will increase to about 2.0 trillion cubic feet annually by 1980 (Table III). In the longer term future, the degree of precision in any forecast is even less clear, but numerous companies have indicated that certain additional projects are under "active consideration" or "investigation". On this basis the growth rates expected in the 1975-1980 period should continue into the decade of the 80's, thus yielding a projected LNG availability of about 4 trillion cubic feet annually by 1990.

Gas From Coal

Progress toward the development of improved processes to
produce high - B.t.u. synthetic pipeline quality gas from coal can
currently be seen on several fronts. Two large-scale coal gasifi-
cation pilot plants are currently in operation or under construc-
tion and plans to build two others have been firmed up. The
pilot plant in operation is located near Chicago, Illinois, and
employs the HYGAS process developed by the Institute of Gas
Technology. A plant using the Consolidation Coal Company CO_2
Acceptor process is nearing completion at Rapid City, South Dakota.
The Department of the Interior has awarded a contract to Bituminous
Coal Research to build and operate a pilot plant based on their
BI-GAS process near Homer City, Pennsylvania, and construction on a
fourth pilot plant, intended to study the Bureau of Mines' SYNTHANE
process, is scheduled to begin in September of 1972 in suburban
Pittsburgh, Pennsylvania. The research and development work associ-
ated with these new coal gasification processes is not expected to
be completed prior to the late 1970's.

In addition, two other major efforts have been announced to
develop coal gasification facilities in northwestern New Mexico.
These proposed plants would be based on an extension of the Lurgi
technology which has been used in Europe for many years. The
first is a project proposed by El Paso Natural Gas Company, and
the second is a proposal by a consortium composed of Pacific
Lighting Service Company, Texas Eastern Transmission Corporation,
and Utah International Inc. Each of these projects calls for the
construction of one or more gasification plants capable of produc-
ing about 250 million cubic feet per day each and would utilize
some of the extensive coal reserves of the area.

The first few commercial coal gasification plants will prob-
ably be based on Lurgi technology, and the first of perhaps
several Lurgi type facilities could be producing synthetic gas in
commercial quantities by 1976. By 1980 the newer gasification
processes will likely have been fully demonstrated which will
permit the significant expansion and development of a coal gasifi-
cation industry in the period beyond 1980. Several factors will
bear heavily upon the rate of growth which can be attained by this
new industry. Among these are the availability of substantial
tonnages of coal for conversion, the tremendous capital expendi-
tures which will be required for gasification plants and the
supporting mining facilities, and the problems associated with
locating the mine-plant complexes in areas able to provide the
necessary uncommitted coal reserves as well as the required process
water.

With these factors in mind the availability of pipeline
quality gas from coal may be projected to rise from about 0.1

trillion cubic feet in 1976 to 0.3 trillion cubic feet annually by
1980 with these volumes most likely entirely attributable to Lurgi
type plants. Gas available from added facilities based on the
newer process technologies currently under development is projected
to bring the total annual volumes of gas available from coal gasifi-
cation to about 1.4 and 3.3 trillion cubic feet, respectively, in
years 1985 and 1990.

Gas From Alaska

The year-end 1971 proved reserves of natural gas in Alaska were
31.4 trillion cubic feet. Of this amount about 26 trillion cubic
feet are attributable to the Prudhoe Bay area of the North Slope.
It is widely known, however, that because the North Slope gas reserves
are chiefly associated-dissolved volumes related to the North Slope
oil reserves, this gas can become available to market only as pro-
vision for the production of the oil is provided. Any projection of
the availability of North Slope gas to the markets of the lower 48
states is therefore heavily dependent on the availability and tim-
ing of a transport capability for both the oil and the gas.

A great deal of planning, research, engineering and other
preliminary work with respect to a Trans-Alaska oil pipeline has
already been completed. However, considerable delays in the initia-
tion of construction of the proposed pipeline have been encountered
chiefly as a result of the environmental implications of the project.
For the purpose of this projection, further delays are assumed to
be minimal and oil production from the North Slope is assumed to
begin in 1976.

Three major proposals have been advanced which would provide
large diameter pipeline transportation for North Slope gas as well
as that gas which may become available in Canada's Northwest fron-
tier areas. The Gas Arctic Systems group has proposed a 1550 mile
system which would connect the Prudhoe Bay area with an extension
of Alberta Gas Trunk Line's existing system in Alberta, Canada.
This system could make gas available to U.S. Westcoast and Midwest
markets through pipeline interconnections with existing pipeline
systems. Sponsors of the Mountain Pacific Project have proposed the
construction of a system passing from the North Slope area through
the Fort Liard region of the Northwest Territories and then south-
ward through British Columbia to the international border where it
would connect with a newly proposed U.S. carrier and serve Pacific
coast markets as far south as Los Angeles. A third proposal,
advanced by the Northwest Project Study Group, would provide a 2,500
mile line extending from Prudhoe Bay to the Canadian-U.S. inter-
national boundary near Emerson, Manitoba. Whichever line is
ultimately built will likely be capable of moving approximately
three billion cubic feet of gas daily when fully powered.

     The projection of the availability of Alaskan gas (Table III)
is based on the assumption that a gas pipeline system traversing
Canada will be completed for initial service in late 1976 or in 1977.
Although the timing of current plans to provide for the pipeline
movement of North Slope oil and gas is subject to considerable con-
jecture, a projection of 0.7 trillion cubic feet of Alaskan gas in
1980 is reasonable. Alaskan natural gas production and transmission
capability should expand to 1.3 and 2.3 trillion cubic feet annually
by 1985 and 1990, respectively. These projections exclude those
Canadian volumes which may be transported in the same pipeline system;
all Canadian gas has been included with the projection of Canadian
imports.

CONCLUSIONS

     Our projection of the United States' gas supply-demand balance
through 1990 is summarized in Table IV and Figure 8. The availabil-
ity of gas from all sources is expected to fall increasingly behind
demand. An annual unsatisfied demand for gas of about 9 trillion
cubic feet by 1980 will increase to about 17 trillion cubic feet by
1990. Domestic production of natural gas is projected to peak in
the mid-1970's and fall slowly thereafter, placing an increasingly
heavy future reliance on imports and other supplemental gas supplies.
While this outlook may appear to be pessimistic, it is not predica-
ted on a pattern of failure. The future prospects for domestic
reserve additions, pipeline and LNG imports, Alaskan gas, and synthet-
ic gas from coal have been carefully analyzed and a reasonably
successful program of development and implementation for each has
been assumed. The purpose of these projections has been to approx-
imate the likely national supply-demand balance over the period
considered and to establish some idea of the probable supply-demand
posture which the Nation can expect. If these projections portray
the future course of events with any degree of accuracy, it is
obvious that solutions to the Nation's gas supply problem or a
significant modification of the anticipated supply-demand balance
will not be simple or swift.

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Table I

UNITED STATES NATURAL GAS SUPPLY EXCLUDING ALASKA
1950-1971
(Volumes in Tcf)

Year	Net Production (1)	Reserve Additions (2)	Year-End Reserves (3)	R/P Ratio (3)/(1) (4)	F/P Ratio (2)/(1) (5)
1950	6.9	12.0	184.6	26.8	1.7
1951	7.9	16.0	192.8	24.4	2.0
1952	8.6	14.3	198.6	23.1	1.7
1953	9.2	20.3	210.3	22.9	2.2
1954	9.4	9.6	210.6	22.4	1.0
1955	10.1	21.9	222.5	22.0	2.2
1956	10.9	24.7	236.5	21.7	2.3
1957	11.4	20.0	245.2	21.5	1.8
1958	11.4	18.9	252.8	22.2	1.7
1959	12.4	20.6	261.2	21.1	1.7
1960	13.0	13.8	262.2	20.2	1.1
1961	13.4	16.4	265.4	19.8	1.2
1962	13.6	18.8	270.6	19.9	1.4
1963	14.5	18.1	274.5	18.9	1.2
1964	15.3	20.1	279.4	18.3	1.3
1965	16.3	21.2	284.5	17.5	1.3
1966	17.5	19.2	286.4	16.4	1.1
1967	18.4	21.1	289.3	15.7	1.1
1968	19.3	12.0	282.1	14.6	0.6
1969	20.6	8.3	269.9	13.1	0.4
1970	21.8	11.1	259.6	11.9	0.5
1971	21.9	9.4	247.4	11.3	0.4

Source: American Gas Association

Table II

UNITED STATES DOMESTIC SUPPLY AND DEMAND
1972-1990
(Volumes in Tcf)

Year	Demand	Production	Domestic Supply Deficit
1972	26.1	23.8	2.3
1973	27.7	24.7	3.0
1974	28.8	24.8	4.0
1975	29.8	24.7	5.1
1980	34.5	20.4	14.1
1985	39.8	18.5	21.3
1990	46.4	17.8	28.6

Table III

SUPPLEMENTAL SUPPLIES OF NATURAL GAS
Projected 1971-1990
(Volumes in Tcf)

Year	Pipeline Imports	LNG Imports	Gas From Coal	Alaskan Gas	Annual Total
1970	0.8	*	-	-	0.8
1971	0.9	*	-	-	0.9
1972	1.0	*	-	-	1.0
1973	1.1	*	-	-	1.1
1974	1.1	*	-	-	1.1
1975	1.2	0.3	-	-	1.5
1980	1.6	2.0	0.3	0.7	4.6
1985	1.9	3.0	1.4	1.3	7.6
1990	1.9	4.0	3.3	2.3	11.5
Total	31.1	38.0	17.3	20.6	107.0

*Small Volumes

Table IV
UNITED STATES GAS SUPPLY-DEMAND BALANCE
Actual 1966-1970; Projected 1971-1990
(All Volumes in Trillions of Cubic Feet @ 14.73 Psia and 60° Fahrenheit)

Year	Annual Demand	Net Pipeline Imports 1/	LNG Imports	Gas From Coal	Gas From Alaska	Gas From Liquid Hydrocarbons	Domestic Production	Annual Consumption	Un-Satisfied Demand	Reserve Additions	Year-end Reserves	R/P Ratio
1966	17.9	0.4	-	-	-	-	17.5	17.9	0.0	19.2	286.4	16.4
1967	18.8	0.5	-	-	-	-	18.4	18.8	0.0	21.1	289.3	15.8
1968	19.9	0.6	*	-	-	-	19.3	19.9	0.0	12.0	282.1	14.6
1969	21.3	0.7	*	-	-	-	20.6	21.3	0.0	8.3	269.9	13.1
1970	22.6	0.8	*	-	-	-	21.8	22.6	0.0	11.1	259.6	11.9
1971	24.6	0.9	*	-	-	**	22.8	23.7	0.9	12.0	248.8	10.9
1972	26.1	1.0	*	-	-	**	23.8	24.8	1.3	13.0	238.0	10.0
1973	27.7	1.1	*	-	-	**	24.7	25.8	1.9	14.0	227.3	9.2
1974	28.8	1.1	*	-	-	**	-24.8	25.9	2.9	15.0	217.4	8.8
1975	29.8	1.2	0.3	-	-	**	24.7	26.2	3.6	16.0	208.7	8.4
1980	34.5	1.6	2.0	0.3	0.7	**	20.4	25.0	9.5	17.0	186.1	9.1
1985	39.8	1.9	3.0	1.4	1.3	**	18.5	26.1	13.7	17.0	175.4	9.5
1990	46.4	1.9	4.0	3.3	2.3	**	17.8	29.3	17.1	17.0	170.4	9.6
1971-1990 Totals	707.6	31.1	38.0	17.3	20.6	**	414.2	521.2	186.4	325.0	-	-

* Very small volumes
** Insufficient data for quantitative projection: unsatisfied demand will be reduced by the amount of SNG actually produced.
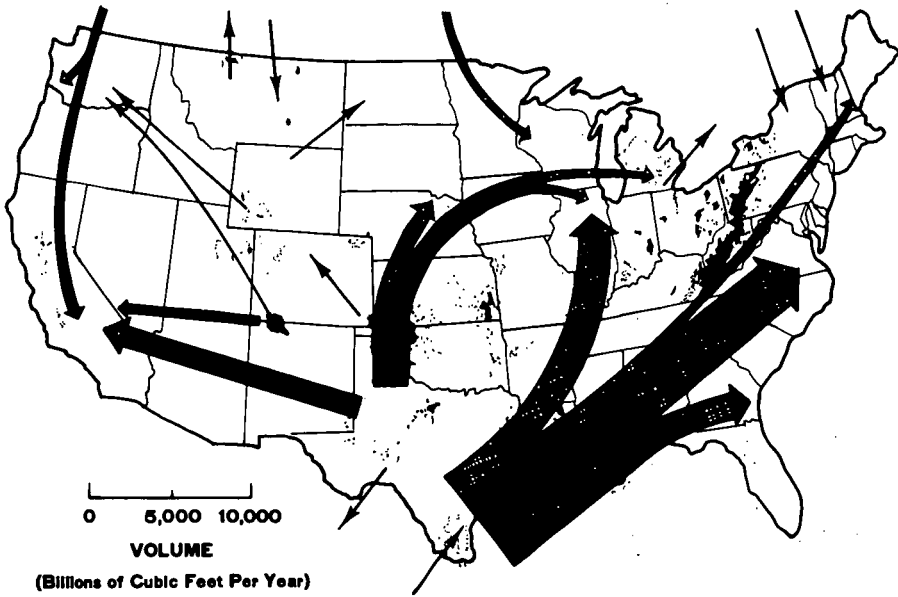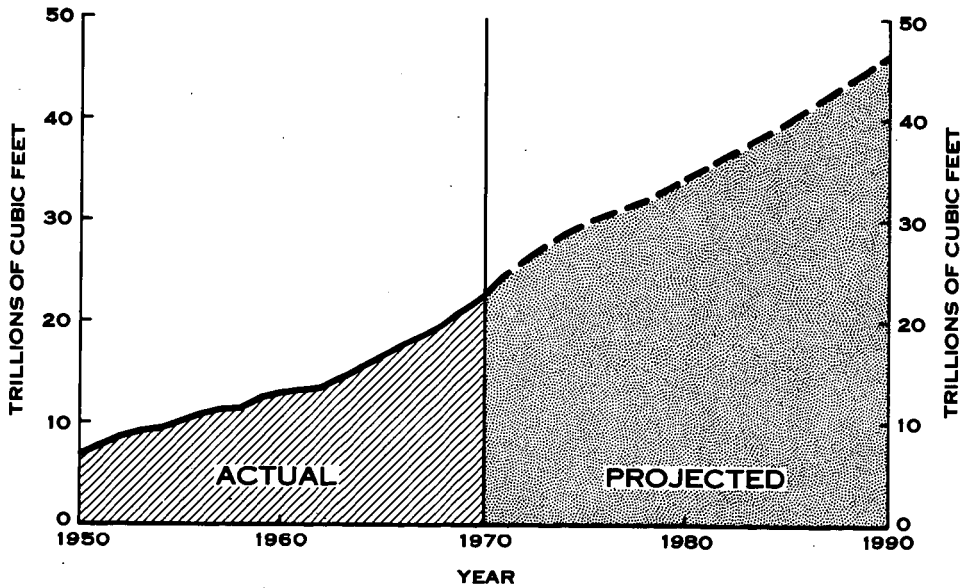1/ Contiguous 48 states.

1970 INTERSTATE NATURAL GAS MOVEMENTS

VOLUME

(Billions of Cubic Feet Per Year)

Figure 1

DEMAND FOR NATURAL GAS

Figure 2

NATURAL GAS PRODUCTION AND RESERVE ADDITIONS
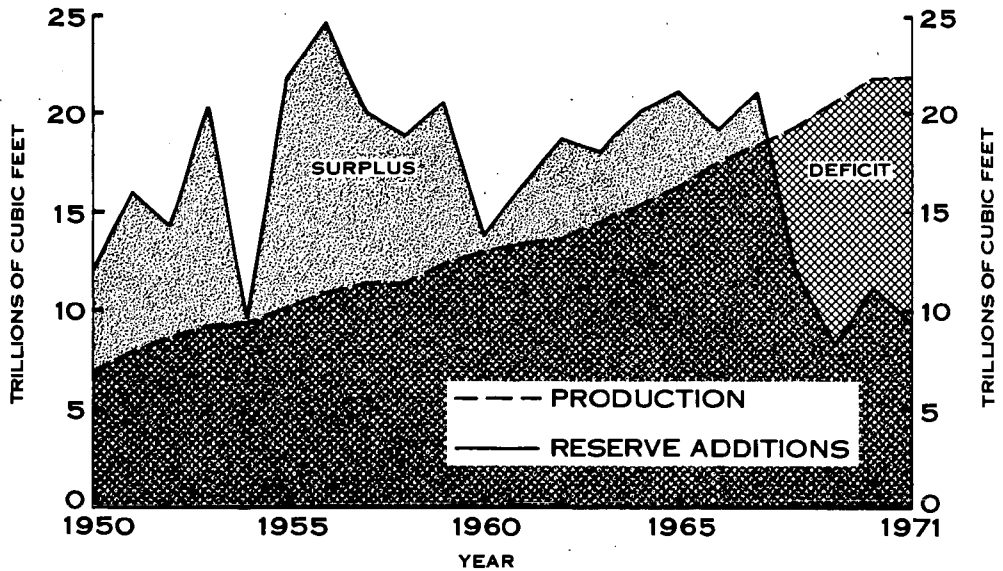
Figure 3
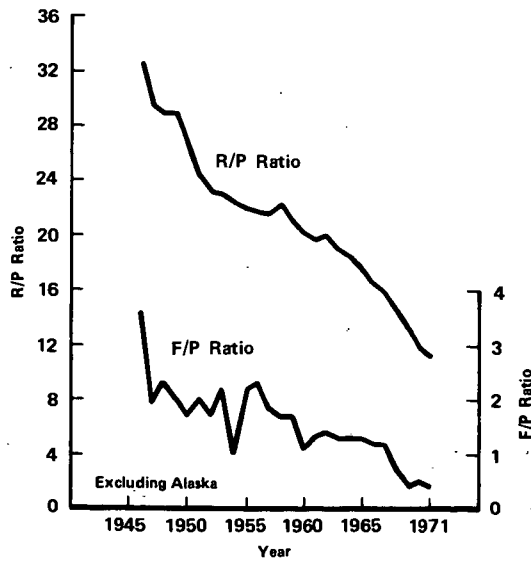

Figure 4

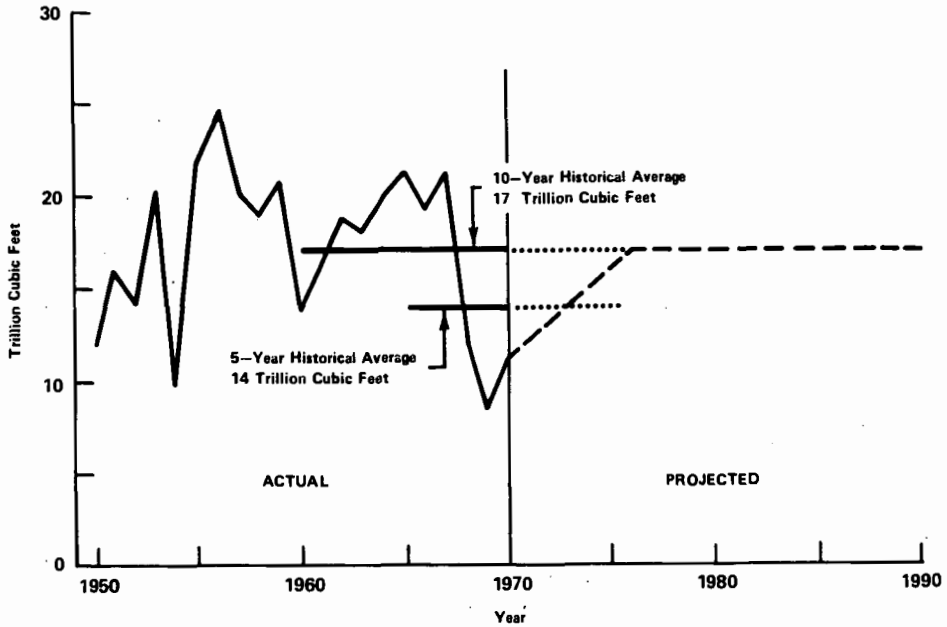ACTUAL AND PROJECTED NET RESERVE ADDITIONS
(CONTIGUOUS 48 STATES)

Figure 5

ACTUAL AND PROJECTED
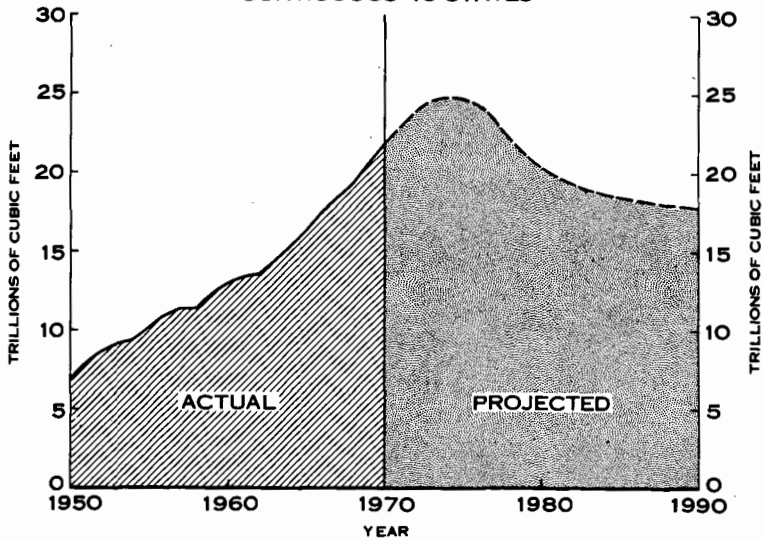## DOMESTIC PRODUCTION OF NATURAL GAS
CONTIGUOUS 48 STATES

Figure 6

LEVELS OF DOMESTIC PRODUCTIVE CAPACITY
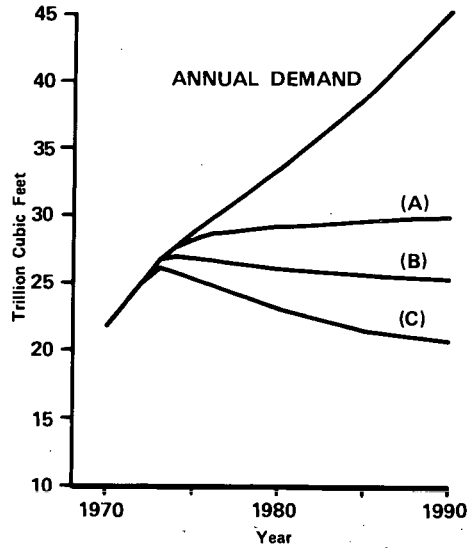WITH ANNUAL RESERVE ADDITIONS OF:
(A) 30 Tcf   (B) 25 Tcf   (C) 20 Tcf

Figure 7

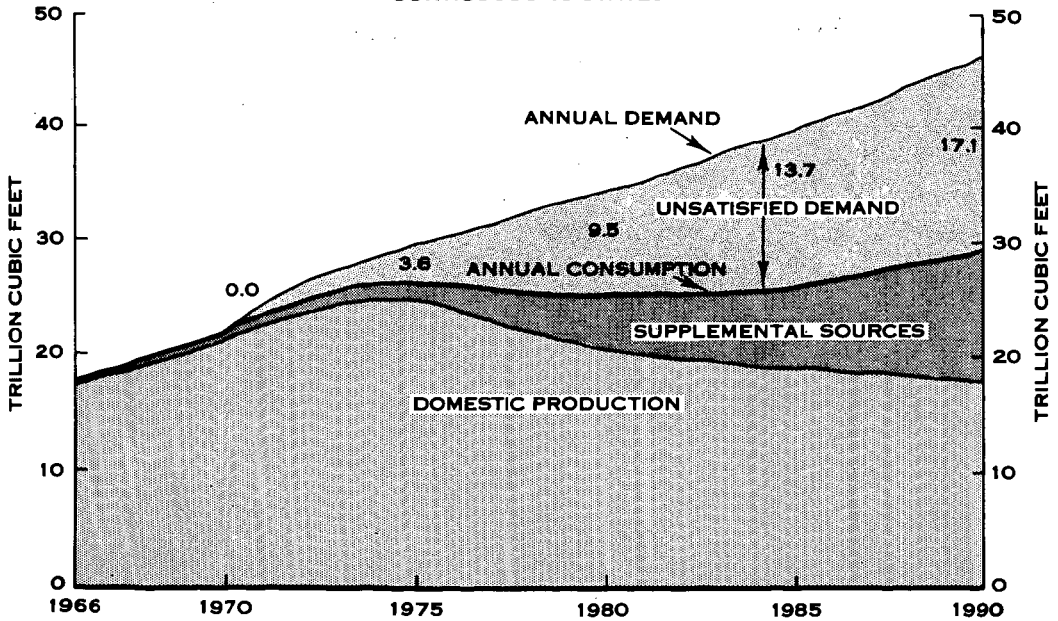# UNITED STATES GAS SUPPLY-DEMAND BALANCE
CONTIGUOUS 48 STATES

Figure 8

Low Sulphur Coal Supplies for Environmental Purposes

Thomas W. Hunter

Division of Fossil Fuels, Bureau of Mines,
United States Department of the Interior
Washington, D. C.

As the agenda of this symposium emphasizes national concerns with regard to the adequacy of supplies of all forms of fuel, consistent with environmental requirements, it is essential that coal be placed in perspective vis-a-vis other energy sources, and with regard to the many problems associated with its availability both as a solid fuel and in converted form.

The vital role that coal must play if the Nation's energy requirements are to be met, and if a sound balance is to be achieved between indigenous and foreign sources of energy supply, is underscored by the serious need for supplemental supplies to meet the insatiable demands being made on natural gas, the decline in proved indigenous oil reserves, and increasing dependence on imported oil, with its consequent implications on national security. Equally significant is that economic, technologic, and societal problems also are delaying the availability of large-scale nuclear power availabilities.

Although environmental concerns cover a broad spectrum of considerations, anxieties with respect to the adequacy of supplies of low-sulphur coals, and of other coals for which utilization can be made viable for environmental purposes through chemical processing and other new technologies, center principally around the enormously increasing needs of electric utilities for their basic energy supplies. Closely related are the relative availabilities of the other energy sources and the extent to which low-sulfur coals are held, and used, for coke production for steelmaking both at home and abroad.

There is no question regarding the enormity of our coal resources, particularly as compared to the relatively limited resources of our other indigenous energy fuels, nor even with respect to our large reserves, per se, of low-sulphur coals. There are many problems involved in the availability of the latter, however, including their extent and location; strong deterrents to, or lack or incentives for, the development of substantially increased capacity for their production; the extent of their need in relation to potential availabilities of other energy supplies, including imports; the development of technologies to condition our high-sulphur coals to meet environmental standards; and increasingly severe sulphur content limitations which correspondingly narrow even the low-sulfur coal resource base.

Although in the interplay of economic forces coal's percentage contribution to electric power generation has declined, from 1955 to 1970 tonnages consumed increased from 141 million to 320 million tons. Notwithstanding optimism for power generation from other sources, it has been estimated that there will be a need for between 800 million and 1 billion tons of coal for electric power generation by the end of the century if the Nation's total demand is to be satisfied.

Will we be able to provide low-sulphur coal in this magnitude, or its equivalent through process technology, for power generation alone by the year 2000? And what will the availabilities be in the near-term and intermediate periods?

Environmental requirements, rules, and regulations are now! The magnitude and complexities involved are compounded by the relative suddenness with which they have been promulgated, and by their progressively severe limitations. Rather abruptly, and with little time for adjustment, we have been brought to the realization that the large reserves of our great energy resources--upon which our national strengths and social attainments were built and our expectations for the future predicated--no longer are as abundantly usable as in the past. Because of evolving social concepts our energy resource base is being sharply reduced. The name of the game today is quality, not quantity.

As patterns of control already have been set, it is essential that we have more detailed and accurate information on the extent, nature, and location of our low-sulphur coal reserves, and some indication of their relative costs to consumers. Incentives must be provided for the development of substantially increased productive capacity, and for providing the transportation facilities that will be required in the movement of these coals to markets. Also, new technologies of combustion will be required to meet differences in quality characteristics.

Whatever the reserves, the availability of mining capacity will be the major determinant of the availability of low-sulphur coal--and at the present time there are many strong deterrents to capital investments in increased capacity, especially in the East. Principal among these are uncertainties regarding the growth and timing of nuclear power generation and of utility commitments thereto, regardless of relative costs; increased oil imports; increasingly severe air pollution regulations; and some expectations that stack gas emission processes to permit the use of high-sulphur coals will obviate the need for heavy investments in new capacity for low-sulphur coal production. As a result, in recent years the great preponderance of new deep mine commercial capacity has been developed only under long term contracts. Since large underground mines are developed for a life span of 20 to 30 years, contractual assurances of continuing markets will be necessary to encourage investment of the many millions of dollars that will be required for the development of large-scale increases in capacity. Essentially, this means long term contracts with electric utilities.

Another important factor in the availability of coal is an adequate supply of transportation facilities, particularly of railroad hopper cars. As there is little or no storage at the mines, except for unit train shipments, mines generally cannot operate without an adequate supply of coal cars, which determine the number of days of active mine operation. Because of the close affinity of coal and rail transportation, the deterrents to expanded coal productive capacity also affect the development of new transportation facilities. Of considerable importance in the future will be an increase in the number of unit trains, which help to reduce transportation costs and which have contributed significantly to the shipment of low-sulphur coals from the West into Midwestern markets; and the potentials for more coal slurry pipelines and "mine-mouth" generating plants. An impressive change in energy transportation in recent years has been the increasing transmission of coal-produced power from generating plants located in or near the coalfields. Only a few thousand miles of extra-high voltage (EHV) transmission lines 10 years ago were increased to nearly 26,000 miles of lines by the end of 1970, and current construction plans call for an increase to approximately 60,000 miles within this decade.

Among the major problems of low-sulphur coal supply is the uneven distribution of reserves in relation to demand. Although major markets are in the East and Midwest, the largest reserves are in the West. Based on preliminary studies by the Bureau of Mines, it is estimated that there are 251 billion tons of low-sulphur coal reserves at less than 1,000 feet in depth, of which an estimated 198 billion tons are in the West and 53 billion tons East of the Mississippi River. Of these totals, 30 billion tons are considered to be low-sulphur strippable reserves in the West at less than 100 feet deep and 2 billion tons in the East. Preponderantly, the low-sulfur reserves are at depths which would require underground mining (168 billion tons in the West and 32 billion tons in the East). Approximately 50 percent of these quantities is recoverable in mining. Supplemental surveys and analyses are being made by the Bureau of low-sulphur coal reserves and production, separately for both the Appalachian region and the rest of the country.

The low sulphur coals of the East are located primarily in the Southern Appalachian region (mostly in West Virginia, Virginia, and eastern Kentucky, with smaller amounts in Pennsylvania, Alabama, and Tennessee). There is very little low-sulphur coal in the Midwest, which is a major area of electric power generation and other coal consumption. Even with washing, the high-sulfur coals indigenous to the Midwest generally are above the sulphur limits of air pollution regulations in most States. Under current technology only the pyritic sulphur can be removed from the coal by conventional methods. Accordingly, to conform to regulations governing coal consumption, the huge markets of the Midwest will have to rely on the Southern Appalachian and Western areas for low-sulphur coal supplies, or on indigenous or other higher-sulphur coals through the use of stack emission processes or other technological developments, including coal conversions to gaseous or liquid fuels.

In the East, most of the low sulphur coal produced customarily has been used for the production of coke for steelmaking, both at home and abroad. Primarily this is because of its high cost as compared to coals heretofore used for power generation. Much of the latter has been lower cost strip-mined coal, whereas in the low-sulphur coal areas production is preponderantly from deep mines which have higher costs and which are at longer distances from consuming markets. Also, because of quality characteristics other than sulphur content, such as differences in ash fusion, many of the coals are not usable in the combustion facilities of some utilities. Accordingly, for power generation in the East under environmental regulations there will be limited supplies of low sulphur coal for some time unless and until there is a substantial increase in mining capacity, supported by contracts with utilities.

Because of the large low-sulphur coal reserves in the West, Western coals have significant potentials for becoming major suppliers to Midwestern and other easterly markets, as well as in their own areas. As an example, owing to the use of unit trains, coal now moves from Montana into Chicago and other Midwestern areas, shipments that were unthinkable only a few years ago. Although these coals are of lesser Btu content than the low-sulphur coals of the East, they are largely strip-mined coals and are appreciably less costly to produce. In addition to unit trains there also are potentials for movement by pipeline, and for the transmission of coal-produced energy by EHV. Coal slurry pipelines have proved their practicability, the best current example being the 275-mile line from the Black Mesa coalfield in Arizona to the Mohave Power Project in Nevada. Also, there are future potentials for the transmission of synthetic coal gas into markets far distant from the coal and synthetic gas producing areas.

Just as air pollution regulations are resulting in significant shifts in consumer sources of coal supply, there also will be drastic changes in the pattern of coal production as demand shifts steadily from high-sulphur to low-sulphur coal areas--until such time as the use of high-sulphur coal becomes permissible through the use of stack emission processes or other technologies, or unless it is found that environmental standards need not be as stringent in some areas as initially considered. The interim economic and social effects on communities in high-sulphur coal areas can be drastic. Some States already require extreme reductions in the level of sulphur content over relatively short periods of time, and although other States presumably have the prerogative of determining their own requirements, they will be under the influence of rather strong Federal guidelines. The EPA recently stated that about half of the new State standards limit the sulphur content of coal to less than 0.8 percent, even though they say at the same time that not enough low-sulphur coal supply is projected to meet these requirements.

The factor of security of supply in both civilian and defense emergencies seems to be a relatively minor consideration, both in some consumer planning and environmental considerations. As costs may be a determining factor for consumers in this respect, comprehensive studies should be made of the relative costs, at points of consumption, of the respective clean energy sources.

Sample transportation studies being made by the Bureau of Mines indicate that there may be some significant price differences in favor of coal as compared to other energy sources, even in the shipment of Western coals farther eastward than Illinois.

Fundamentally, our national concerns for the environment are fully justifiable. While they should not be unnecessarily stringent, regulations should be as strong as is shown to be necessary by factual appraisal. The overall objective must be to preserve, or even improve, the environment while at the same time attaining other social goals without severe disruption to the production, distribution, and utilization of our energy resources. This requires both judgment in the determination and application of controls, and full speed ahead in the development of new technologies to bring about a favorable balance.

In summary, although it is estimated that we have large reserves of low-sulphur coals nationwide, their availability for environmental purposes is fraught with many problems. Among the most significant of these are that their location and markets are largely in contraposition; there are strongly adverse economic influences and consumer preferences, particularly in the East, that militate against the development of heavily increased productive capacity; and the extension of controls increases demand while progressively severe restrictions sharply narrow the range of availabilities as they trend toward sulphur levels that are practicably unattainable. Accordingly, it is anticipated that the supply of low-sulphur coals for environmental purposes will continue to be tight for some time to come.

The Supply of Oil for Future U.S. Needs
and the Subsequent Effects on the Environment

Gene P. Morrell, David R. Oliver, and J. Lisle Reed, Office of Oil and Gas, Department of the Interior, Washington, D. C.   20240.

Throughout most of this century, the United States has been self-sufficient in petroleum supply; however, since 1968 our rate of consumption of oil has been greater than our daily oil production capability. During the present decade, the gap between domestic petroleum demand and domestic production will increase. The gap is a result of several factors: First of all, a seriously insufficient exploration for, and development of, natural gas and crude oil; secondly, the disqualification, for environmental reasons, of much of our high sulfur coal from its normal industrial and utility markets; and finally, a lag in the construction and operation of nuclear electric power plants.

As shown in this first chart, domestic production of crude oil and natural gas liquids appears to be levelling off in this country at slightly over 11 million B/D. The levelling off may even be considered a slightly optimistic projection. Unless present finding and development rates are accelerated, production will soon begin to decline.

With U.S. petroleum demand constantly growing and domestic supply remaining relatively stable, it is proper to assume that this country will look increasingly to other countries for oil. An

important question is, how much foreign oil will be needed and what area of the world will the oil come from? In the projection shown here, 6.5 million B/D will be needed in 1975, and about 10 million B/D in 1980.

There are four major exporting regions in the world: South America (Venezuela); Africa (Libya, Algeria, and Nigeria); Indonesia; and the Persian Gulf countries (Middle East). South American and Persian Gulf oil tend to be high sulfur oil, whereas African and Indonesian oils tend to be low in sulfur. Environmental constraints in this country as well as other countries will probably require most fuel oil to be of low sulfur content. This will probably mean low sulfur crude oil will be sold at a premium price, compared to high sulfur oil, reflecting a cost savings on desulfurization equipment.

It would be difficult to predict at this time exactly where all of our imported oil will come from. But as far as the environment is concerned, it should make little difference because most high sulfur crude oil used in the United States will be desulfurized. If European and Japanese environmental constraints lag behind U.S. criteria, domestic firms, anxious to save the cost of desulfurization, will outbid foreign firms for low sulfur crude. Of course this would accelerate environmental concerns in foreign developed areas since these countries would be left using increasing quantities of high sulfur oil. Therefore, it seems logical that other developed nations

will adopt environmental regulations similar to those that are forthcoming in the United States, and low sulfur crude oil will be distributed throughout the world by other considerations, such as transportation and product yield slates.

There is one other aspect that should be noted at this point. The United States is in a unique and slightly advantageous position compared to other large oil-consuming countries. Much of our domestic crude oil production in East Texas and Louisiana is low in sulfur. This will afford our domestic refineries some additional flexibility in optimizing the use of low sulfur oil, high sulfur oil, and desulfurization facilities.

In the second figure crude oil producing areas of the world are depicted and the areas are drawn in proportion to their known reserves. The crude oil production in all regions except the Persian Gulf is committed for consumption, due either to proximity to a consuming area or qualify of the oil. The crude oil production in these areas is insufficient to meet world consumption needs; because of this, most of our additional imports, as well as the rest of the importing countries' crude oil, will come from the Persian Gulf.

Before leaving the subject of crude oil supply and demand,
I am obligated to point out some problems concerned with projecting
the quantity of oil that will be imported. Referring to the first
figure that was discussed, an oil supply/demand balance was presented.
The imports that are necessary for the country can be calculated
by the difference in estimated oil demand and domestic oil supply.
This sounds simple enough, but other factors affect and complicate
the issue.

Figure 3 displays the total energy supply/demand balance for the
United States for the present century. As can be seen, oil is a large
part of the total energy picture. More importantly, it is also the
alternate or "swing" source of energy. If there are shortfalls in
the development and utilization of nuclear, gas, or coal, oil will be
required to fill the gap.

Projections concerning the timing and quantity of coal,
gas and nuclear development vary greatly. For instance, in figure 4,
projections by Interior's Bureau of Mines, the Federal Power
Commission and the National Petroleum Council, are given for domestic
natural gas production. These gas projections appear on the surface
to be quite different, but they are consistent with the bases and
assumptions used by each group. The point here is that there
are many things that can happen which will affect the development
of our various sources of energy; several assumptions can be made;
and a lot of personal judgment is involved in anticipating fuels
usage. This results in a very clouded picture of the exact quantity

of oil imports that will be needed for the future. Therefore, it is necessary that I caution against naive use of the oil import projection used in this presentation.

The next topic I wish to comment upon is the form in which the oil will be imported, that is crude oil or refined oil products. At the present time foreign residual fuel oil (a refined product) is, for all practical purposes, freely imported into District I (states on the Eastern Seaboard). However, the domestic refiner is not allowed freely imported foreign crude oil from which to manu- facture residual fuel oil for District I. The domestic refiner has to use higher cost domestic crude oil or foreign crude oil imported pursuant to an oil import quota to manufacture residual fuel oil; this has caused domestically produced residual fuel oil to be at a higher cost and to be noncompetitive. In figure 5 the imports of foreign residual fuel oil over the past decade are shown in comparison with imports of foreign crude oil. As can be seen in the figure, imports of residual fuel oil which were once about 50% of crude oil imports have now exceeded crude oil imports.

Residual fuel oil is a natural and significant product of crude oil. A yield of 50% residual fuel oil can be derived from typical or average crudes and a yield of 25% remains after mild or moderate petroleum refining. The average residual fuel oil yield in U.S. refineries is 5 to 6%. The lack of residual fuel oil

production in the United States is a result of high conversion or
severe refinery processing in a complex refinery configuration.
The utilization of high severity processing in the domestic
petroleum industry, which has resulted in the destruction and
conversion of resid, was originally attributed to the fact that the
resid had to compete with low priced coal and natural gas as burner
fuel. However, from the present time forward, due to the inadequate
development of natural gas and disqualification of certain coal uses,
the lack of domestic residual fuel oil production must be attributed
to the import situation.

The import situation is subject to change, and one possible
change would be to allow domestic refiners imports of foreign crude
oil in proportion to the uncontrolled (freely imported) products that
are manufactured in domestic facilities. This would have the beneficial
effect of allowing refining facilities that may otherwise be built in
foreign countries to be built domestically, and it would reduce the
magnitude of high severity operations that are typical in the U.S.
today. An important question at this point is what would be the effect
on the environment from such an action?

As I see it, there would be two significant results of such an action
and they would have a nil or possibly beneficial effect on the
environment. First of all, there would be more crude oil imported

and less products (resid); however, the total level of oil imported
is unchanged. Oil that is imported and processed is handled and
transferred a little more than oil that is imported and distributed
directly to consumers, but this aspect probably has a nil effect on
the environment. The second result is that there would probably be
more crude oil refined in this country than would otherwise occur. This
additional processing may possibly have a slight beneficial effect on
the environment because it would reduce the need for extreme high
severity processing.

The last point is most significant and can best be illustrated
by observing the last three figures of this presentation. Figure 6
is a very simple schematic of a foreign refinery configuration. The
process equipment is simple: a crude fractionation tower to separate
the crude components, and a reformer to upgrade the naphtha cut into
gasoline. A catalytic cracker is shown, but it is only partially
colored in order to illustrate that it is not really typical for foreign
refineries although there are some in existence. The desulfurizer
depicts new equipment that will be going into many refineries.

The next figure illustrates a simple schematic for a U.S.
refinery configuration. The contrast of the U.S. refinery to the
foreign refinery is apparent; there is a massive amount of equipment
(hydrocracker, coker, alkylation unit and cat cracker) that is

dedicated to converting the residual fuel oil portion of the crude

oil to light products. If, however, the increasing demand for

residual fuel oil is considered, and the domestically produced resid

is made competitive with foreign resid by a change in the oil import

program, a greater yield of resid will be derived.

Figure 8 illustrates the change in refinery configuration

which would result from increased resid production. There would be

a larger crude oil feed rate, thus, a larger crude fractionating

tower. However, many of the light products that were made in the

previous configuration by severe cracking would be derived from

distillation of crude oil. Furthermore, much of the resid produced

by distillation would not be converted, but instead sold as a product.

The net result is that more crude oil would be processed, but there

would be much less processing of product streams. The type of

processing that is reduced is the type that directionally has the

most adverse effect on the environment. The high conversion operations

generally operate at high temperatures which require significant

quantities of fuel and cooling water. Also the processes produce

unsaturate hydrocarbons (naphthalenes) and other organic compounds

(phenols) that are resistant to biodegradability.

The ultimate refinery configuration would approach that of

the foreign refinery. Existing refineries would probably find it advantageous

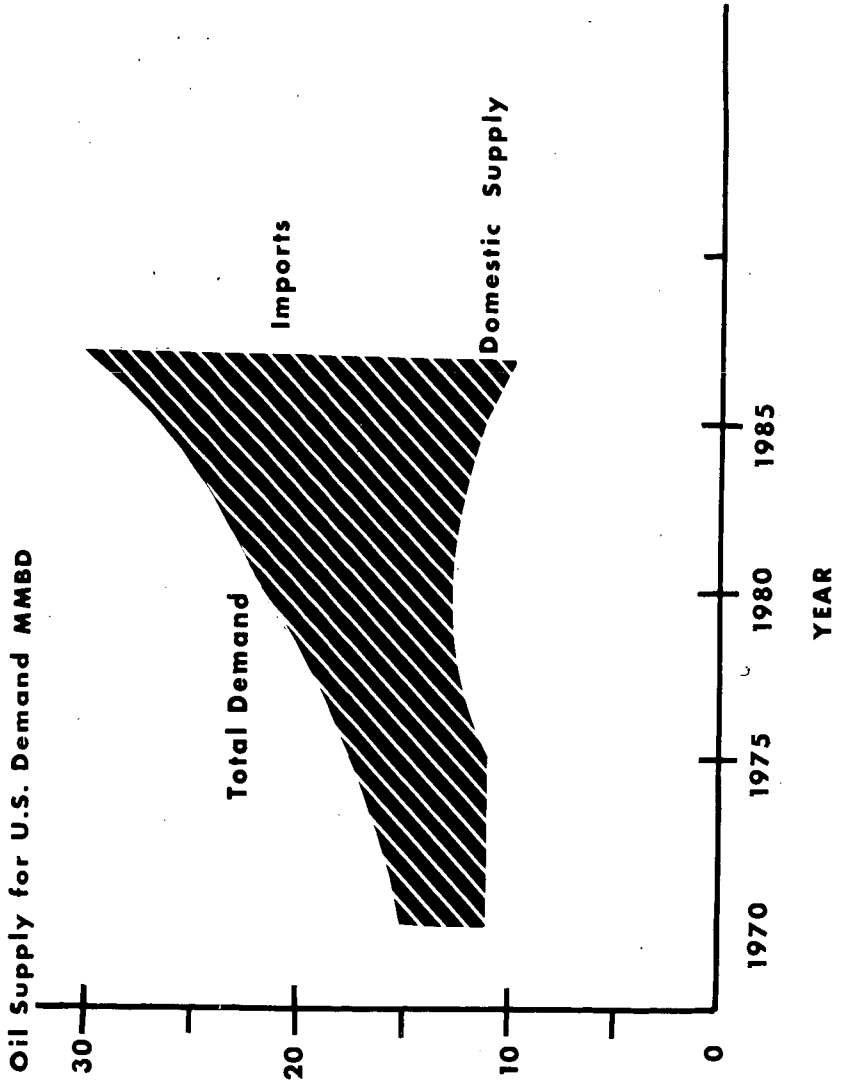to expand the crude fractionation sections and redistribute product streams

to conversion units. The expected result would be a decreased percent conversion for the total crude oil feedstock.

To sum up, we see imports of foreign oil increasing rapidly in this decade. Much of the oil will probably be high sulfur crude oil from the Persian Gulf. We visualize modifications of the oil import program which will enable the refinery equipment, that will process the oil, to be located domestically. This would be beneficial to national security, trade balance, and the domestic economy. The ultimate effect such modifications in the oil import program would have on domestic refinery configurations would probably be slightly beneficial to the environment.

Earlier I referred to the interrelationships of oil, gas, coal and nuclear energy. All these energy sources and the "exotics," which are being developed, will be needed in the future. Yet, Government, as it is presently structured, does not encourage development of a unified energy policy. For example, about 61 Federal agencies are involved in some aspect of oil and gas decisions, and this fragmentation of responsibility can only result in inefficiency.
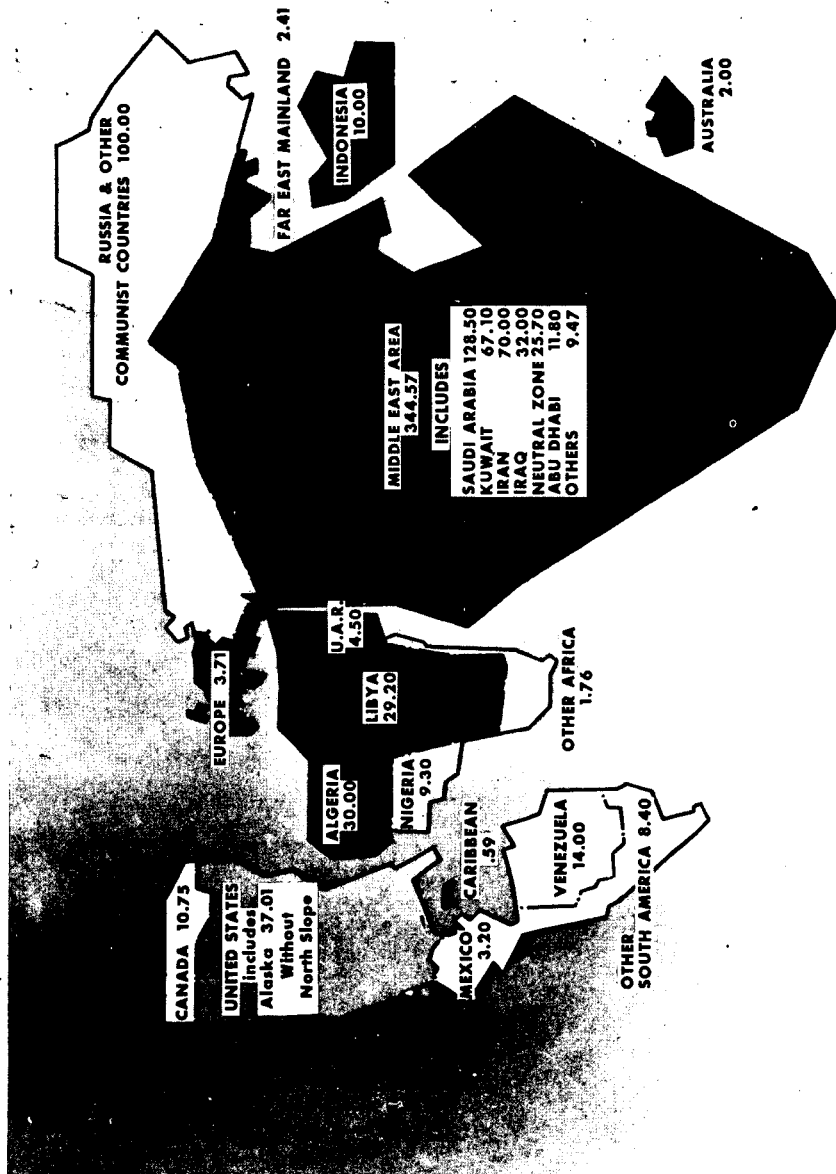
As a first step in overcoming this problem, President Nixon proposed to centralize major energy resource responsibilities in a new Department of Natural Resources. Passage of this legislation is essential if we are to integrate energy conservation and development efforts, and alleviate what more and more people are coming to realize is a serious energy supply problem.

OIL SUPPLY FOR U.S. DEMAND

Oil Supply for U.S. Demand MMBD
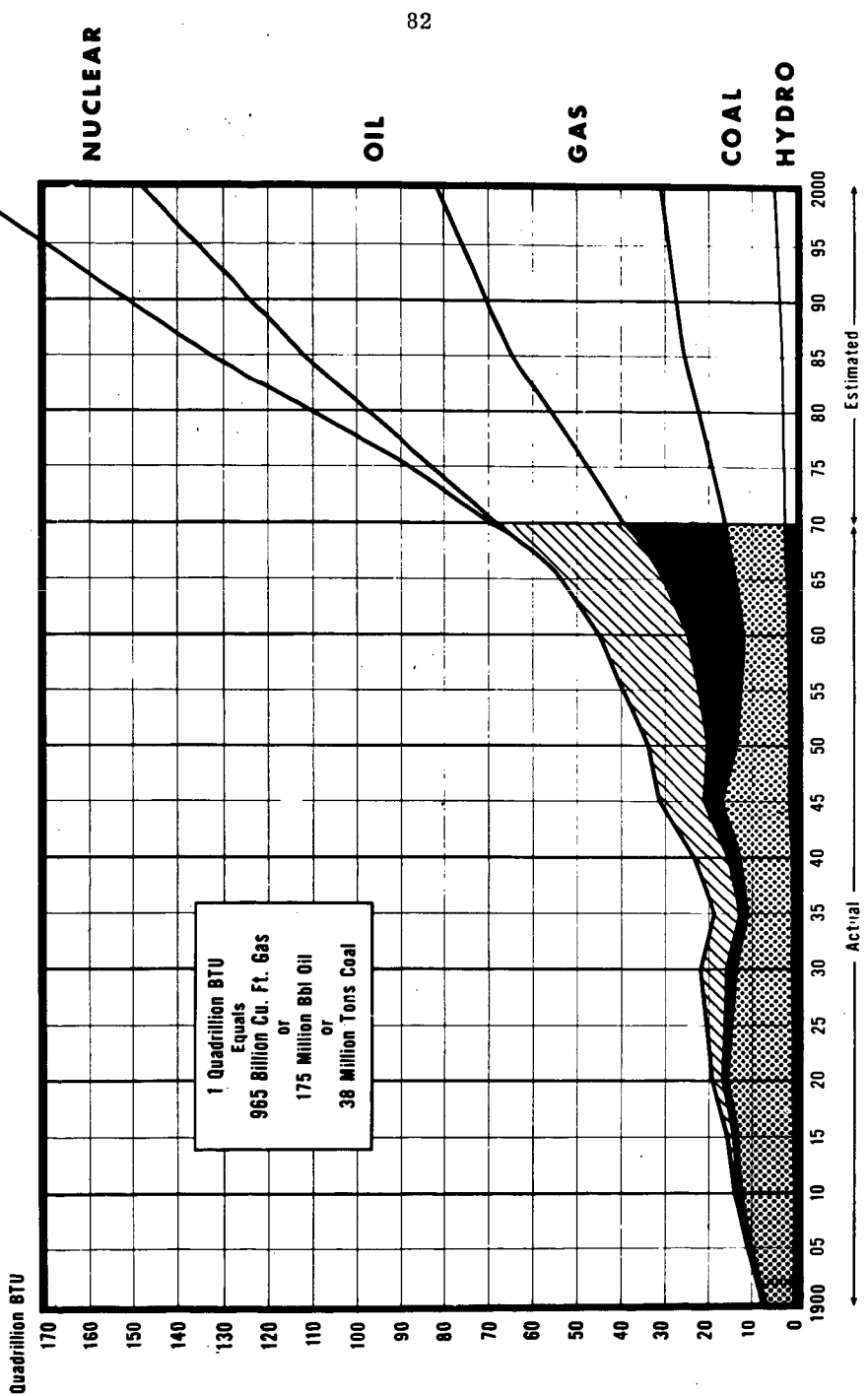
Imports

Domestic Supply

Total Demand

30

20

10

0

1970   1975   1980   1985

YEAR

WHERE THE OIL IS —

WORLD TOTAL 611.40 BILLION BBLS.
AS OF JANUARY 1, 1971

RUSSIA & OTHER
COMMUNIST COUNTRIES 100.00

FAR EAST MAINLAND 2.41

INDONESIA 10.00

AUSTRALIA 2.00

MIDDLE EAST AREA 344.57

INCLUDES

SAUDI ARABIA	128.50
KUWAIT	67.10
IRAN	70.00
IRAQ	32.00
NEUTRAL ZONE	25.70
ABU DHABI	11.80
OTHERS	9.47

U.A.R. 4.50

LIBYA 29.20

OTHER AFRICA 1.76

EUROPE 3.71

ALGERIA 30.00

NIGERIA 9.30

CARIBBEAN .59

VENEZUELA 14.00

CANADA 10.75

UNITED STATES
Includes
Alaska 37.01
Without
North Slope

MEXICO 3.20

OTHER
SOUTH AMERICA 8.40

If geography reflected the reserves of oil in the ground, the map of the world would look like this.

U.S. ENERGY CONSUMPTION IN THE 20th CENTURY

NUCLEAR

OIL

GAS

COAL

HYDRO

Quadrillion BTU

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

1900 05 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 2000

YEARS

Actual ——— Estimated

1 Quadrillion BTU
Equals
965 Billion Cu. Ft. Gas
or
175 Million Bbl Oil
or
38 Million Tons Coal

PROJECTED GAS SUPPLY

Gas Supply, Quadrillion BTU.

Bureau of Mines

Federal Power Commission

National Petroleum Council
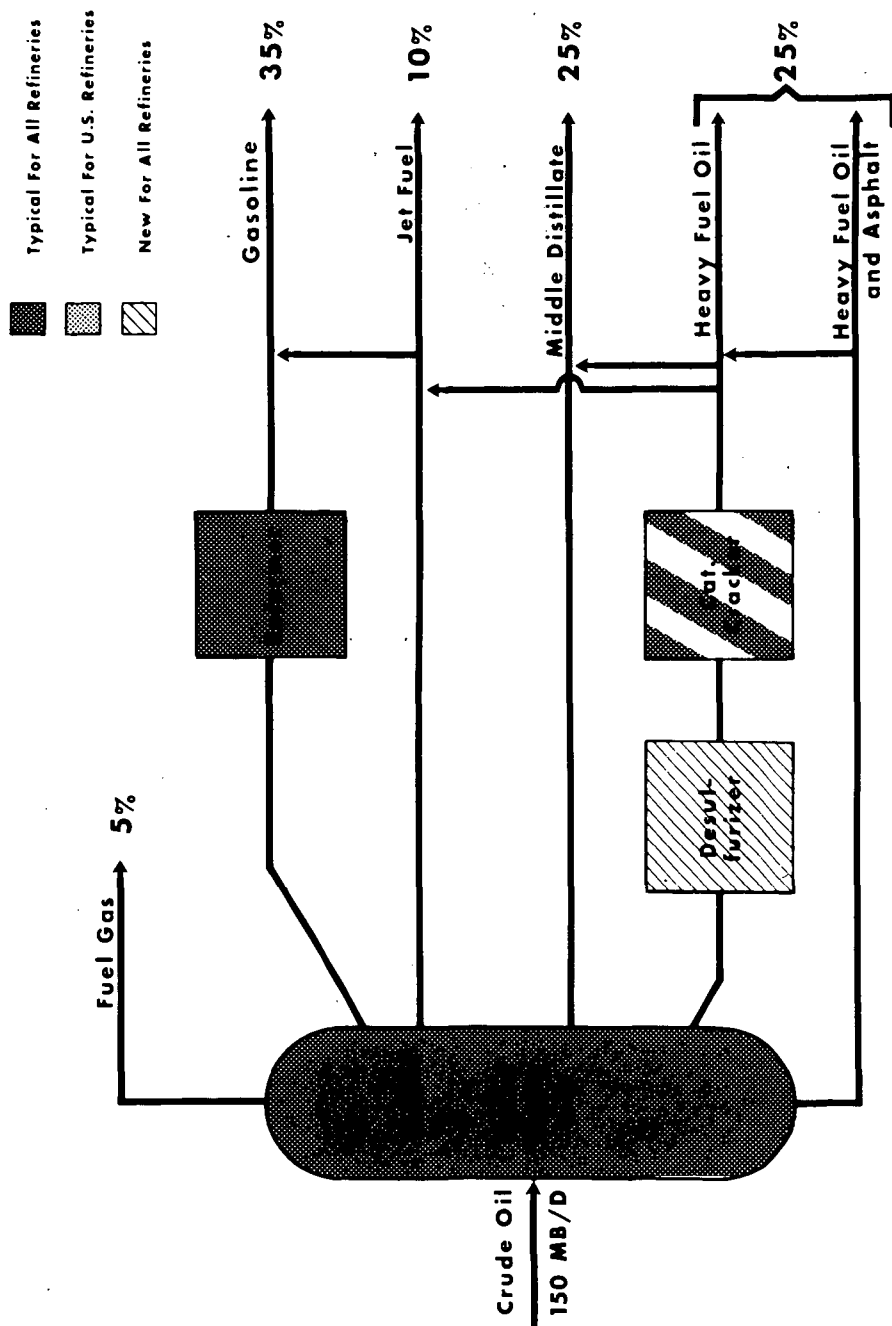
YEAR
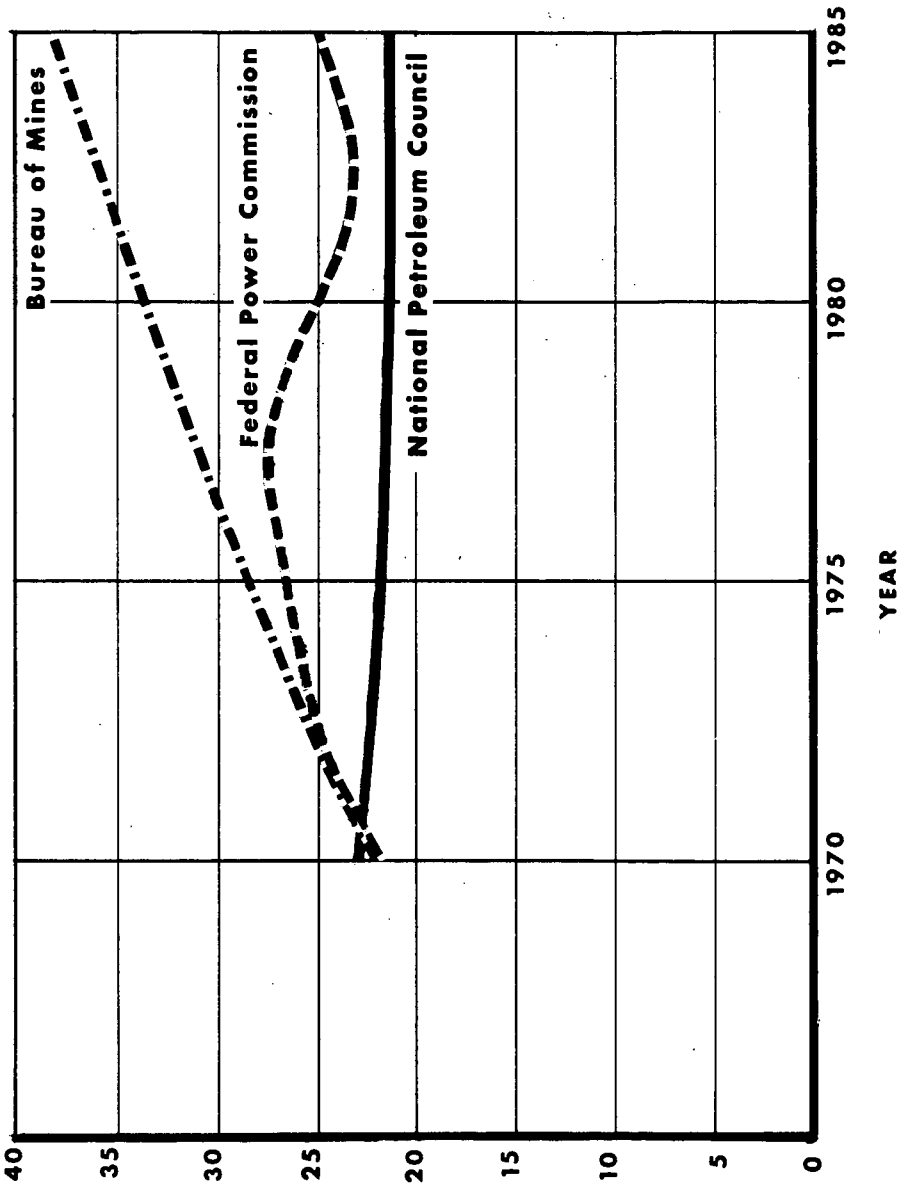
CRUDE OIL IMPORTS COMPARED TO RESIDUAL FUEL OIL IMPORTS

Imports of Resid and Crude Oil, MBD

FOREIGN REFINERY

Typical For All Refineries

Typical For U.S. Refineries

New For All Refineries

Fuel Gas 5%

Gasoline 35%

Jet Fuel 10%

Middle Distillate 25%

Heavy Fuel Oil

Heavy Fuel Oil and Asphalt

25%

Crude Oil 150 MB/D

Desulfurizer

Cat. Cracker

Office of Oil and Gas
Aug. 1971

U. S. REFINERY

Crude Oil
150MB/D

Fuel Gas 5%

Alkylation

Hydro-Cracker

Coker

Desulfurizer

Gasoline 55%

Jet Fuel 15%

Middle
Distillate 15%

Lubes &
Specialties 5%

Heavy Fuel Oil

Heavy Fuel Oil
& Asphalt 5%

Typical For All Refineries

Typical For U.S. Refineries

New For All Refineries

Office of Oil and Gas
Aug. 1971

BALANCED REFINERY

Crude Oil 235 MB/D — Initial Crude Unit

Fuel Gas 5%

Reformer — Gasoline 35%

Jet Fuel 10%

Middle Distillate 25%

Cat. Cracker

Desul-furizer

Heavy Fuel Oil / Heavy Fuel Oil and Asphalt 25%

Typical For All Refineries
Typical For U.S. Refineries
New For All Refineries

Office of Oil and Gas
Aug. 1971

INT: 7397-72

THE DEMAND FOR SULFUR CONTROL METHODS
IN ELECTRIC POWER GENERATION

Robert M. Jimeson

Office of the Advisor on Environmental Quality
Federal Power Commission, Washington, D.C.   20426

INTRODUCTION

This paper examines the features of air quality legislation that have an impact on the demand for sulfur oxide control measures for the power industry; the limitations on sulfur imposed by emission regulations, and the electric power supply situation. Finally, estimates of probable demand are derived for various quality fuels and for sulfur oxide control equipment in the electric power industry in the next several years.

AIR QUALITY REGULATIONS

The Clean Air Act of 1967 called for the designation of air quality control regions by the Federal Government with the consent of the state and with local approval. Furthermore, the Federal Government had to issue for each pollutant, air quality criteria from which standards could be established. It had to issue companion reports on control technology for the reduction of emissions from various sources. Then, state governments were to establish air quality standards for their designated regions and adopt plans for implementation of control programs that would achieve constituted standards.

Under the provisions of the 1967 Act, areas were being designated as control regions in a sequence according to their severity of pollution, proceeding from the worst to the least polluted. This approach appeared to have a built-in mechanism for accelerated and achievable control activity while simultaneously permitting the primary energy supply and control equipment industries to adjust in an orderly and timely manner to a gradual, but intensified, demand for high quality fuels and emission control equipment. However, to some, the procedures appeared too tedious and slow. Consequently, the Clean Air Act as

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Note: The views expressed herein are those of the author and do not necessarily represent the views of the Federal Power Commission.

amended in 1970 was designed to shorten the procedures and hasten the day in which all areas of the Nation would be brought under control, regardless of the current quality of its air. The provisions of this recent legislation accentuate the demand for control equipment and all forms of "clean" energy.

The Clean Air Act as amended in 1970 required that all areas of the Nation be designated very quickly as air quality control regions. Every part of the United States has now become part of an intrastate or interstate air quality control region. There are 237 control regions in the lower forty-eight states. All sources of pollution anywhere in the nation are now subject to regulation; thus, the demand for various control measures is immediately intensified nationwide. The location of the regions and the magnitude of their current pollution problem is shown in Figures 1 and 2.

The legislation also required the Environmental Protection Agency (EPA) to establish national primary ambient air quality standards to protect health and secondary standards to protect the public welfare. Ambient standards were greatly needed as a guide to the degree of emission controls required in various regions. National standards for particulates, sulfur oxides, nitrogen oxides, carbon monoxide and hydrocarbons, and photochemical oxidants were issued in April 1971. The states could set standards within their own boundaries more stringent than those of the Federal Government. However, by July 1975, the states had to achieve air quality equal to or better than the national standards.

The principal pollutants of concern to fossil fuel-fired electric power plants are sulfur oxides, particulates, and nitrogen oxides. The national ambient air quality standards for these three pollutants are shown in Table I.

NATIONAL AMBIENT AIR QUALITY STANDARDS

POLLUTANT	AVERAGING TIME	PRIMARY STD.		SECONDARY STD.	
		$\mu g/m3$	p.p.m.	$\mu g/m3$	p.p.m.
SULFUR OXIDES	Annual	80	0.03	60	0.02
	24 Hour*	365	0.14	260	0.1
	3 Hour*	-	-	1300	0.5
PARTICULATE	Annual	75	-	60	-
	24 Hour*	260	-	150	-
NITROGEN OXIDES	Annual	100	0.05	100	0.05
	24 Hour*	250	0.13	250	0.13

*Not to be exceeded more than once per year.

Table I

By January 30, 1972, each state was required to adopt and to submit to EPA a plan providing for the implementation, maintenance, and enforcement of a program which would enable it to meet the national primary ambient air quality standards within its regions by the middle of 1975. EPA must approve or reject these plans or portions of them by May 30, 1972.

Due to the shortness of time, the states had a tendency to determine the degree of reduction in emissions needed to meet the national or their own more stringent ambient air quality standards for their worst polluted region and then to apply the same degree of reduction to all other regions in the state. Lack of individual regional analysis which tailor regulations to each region's specific needs intensifies the demand for clean fuels and control equipment due to an aggregation of excessive requirements. Non-critical regions are thus put in competition with the critically polluted regions for the limited "clean" fuels and control devices.

EPA also had to establish national emission standards for certain categories of new sources. Table II shows the Federally mandated emission standards for new and modified fossil-fired steam generators. They apply to units with a capacity of 250 million Btu per hour (i.e., about 25 megawatts) or larger for which major construction or modification contracts were signed after August 17, 1971.

STANDARDS OF PERFORMANCE FOR
NEW FOSSIL-FIRED STEAM GENERATORS
(construction commenced after August 17, 1971)

FUEL TYPE	STANDARDS Lbs. per Million Btu		
	PARTICULATE	SULFUR OXIDES	NITROGEN OXIDES
SOLID	0.10	1.2	0.70
LIQUID	0.10	0.80	0.30
GASEOUS	-	-	0.20

Table II

Having examined the air pollution regulations influencing the demand for various quality fuels and for control devices, consider next the Nation's need for electric generation as a factor in the magnitude of the demand for controls.

OUTLOOK FOR ELECTRIC POWER GENERATION

Many of the projections used in this section were taken from the Federal Power Commission's 1970 National Power Survey. More than one hundred experts representing all segments of the electric power industry and branches of government contributed to its contents.

As illustrated in Figure 3 the electric power industry of the United States in 1970 generated nearly eighty-two percent of the electricity in fossil-fueled plants. Almost all of the remainder, except for 1.4 percent produced by nuclear plants, was generated by hydro-power. Nuclear generation is expected to make significant inroads into the generation picture of the next two decades and, consequently, the relative position of fossil-fueled generation will decrease from about 82 percent in 1970 to about 44 percent in 1990.

Figure 4 shows that the electric power industry generated 1.541 billion megawatt-hours in 1970. In the process it consumed approximately one-quarter of all the primary energy used during that year by all segments of the American economy. During the next two decades total electric power generation by electric utilities is expected to about double every ten years. Total generation is estimated to reach 3.11 billion megawatt-hours in 1980 and close to 6 billion megawatt-hours in 1990. In the same period, fossil-fueled generation will increase to about 1.9 billion megawatt-hours in 1980 and about 2.6 billion megawatt-hours in 1990. While fossil-fueled steam plants will supply a decreasing portion of the total as shown in Figure 3 the fossil-fueled units will supply twice as much electric energy in 1990 as in 1970. This is further reflected in projected fossil-fueled capacity additions from 1970 to 1990 shown in Table III.

The fossil-fueled energy was generated at plants having 3298 boiler-generator units with a total steam-electric generating capacity of 259 thousand megawatts. The capacity will increase to 558 thousand megawatts by 1990. Average size of the units will increase from 80 to 370 megawatts and the number of units will decrease to 1520 in 1990.

During the same period, 1970 to 1990, total generating capacity, including nuclear and hydroelectric plants, is expected to nearly quadruple from 340 thousand megawatts to 1260 thousand megawatts--an increment of 920 thousand megawatts.

Some of the 920 thousand megawatts of generating capacity will be re-
quired by the "clean" primary energy and control process industries
sewage treatment plants, incinerators, and others to accomplish the
environmental goals in the fields of air and water pollution control
and solid waste management. Electricity is very necessary for the
achievement of this Nation's environmental goals, and serious thought
must be given to the trade-off of the environmental benefit of the
use of electricity relative to the environmental impacts of its
generation.

In the shorter range projection to the year 1975, when the
state air pollution control programs are to be implemented, Table
III shows that there will be about 2900 fossil-fueled units with
a total estimated capacity of 320 thousand megawatts. The average
size of the fossil-fueled units in operation during that year will
be about 110 megawatts.

U.S. FOSSIL-FUELED STEAM-ELECTRIC CAPACITY

YEAR	CAPACITY MW (Thous.)	NO. OF UNITS	AUG. SIZE MW (Thous.)
1970	259	3,298	80
1975	320	2,900	110
1980	380	2,389	160
1990	558	1,520	370

Table III

The Federal Power Commission, with the cooperation of the
Environmental Protection Agency, collects on FPC Form 67 air and
water quality control data for each fossil fuel-fired electric
generating plant of 25 megawatts and greater. Under this program
the FPC collected information for the year 1969 from 655 fossil-
fueled plants with 2995 boiler-generator units having a total
capacity of 244 thousand megawatts, as compared with the 3298
units with a total capacity of 259 thousand megawatts reported
in Table III for the year 1970.

Form 67 data shows that of the 2995 units surveyed for the
year 1969, 1150 units were primarily coal-fired, 945 units were
primarily oil-fired, and about 900 units were primarily gas-fired.
Assuming that the 303 small units not covered by the Form 67 pro-
gram divide in the same proportions, then the distribution of the
number of units in operation in 1970 by type of fuel fire is shown
in line 1 of Table IV.

PROJECTED MIX OF
FOSSIL-FUELED GENERATING UNITS

	TYPE OF FUEL		
	COAL	OIL	GAS
NUMBER OF UNITS 1970	1265	1045	990
ADDITIONS	+66	+26	+24
Subtotal	1331	1071	1014
RETIREMENTS	-281	-141	-80
Subtotal	1050	930	934
CONVERSIONS	-90	+120	-30
NUMBER OF UNITS 1975	960	1050	904

Table IV

From information reported on April 1, 1971, by the nine
Regional Electric Reliability Councils in response to the Com-
mission's Statement of Policy on Adequacy and Reliability of
Electric Service, Order No. 383-2, the author estimates that
about 116 additional units with 70 thousand megawatts of
capacity might be in operation by the end of the year 1975.
As shown in the second line of the Table, 66 are expected to
be coal-fired, 26 oil-fired, and 24 gas-fired.

There were 1004 fossil-fueled units with a total capacity
of about 18 thousand megawatts which were installed in 1940 or
earlier, but were still in operation in 1970. Some of these
units date back to the first two decades of this century.
These units were an estimated 56 percent coal-fired, 28
percent oil-fired, and 16 percent gas-fired. Assuming that
one half of each of the types of older units will be retired
by 1975, then 281 coal-fired, 141 oil-fired and 80 gas-fired
units will be retired. In addition 90 coal-fired and 30
gas-fired units are expected to be converted to oil-fired.

Consequently, by 1975 there will be 960 coal-fired and
1050 oil-fired for a total of 2010 units which will require
some form of sulfur emission control either through the use

of stack devices for the removal of sulfur dioxide from power plant flue gases or through the use of low-sulfur fuels.

FOSSIL FUEL DEMAND FOR ELECTRIC POWER GENERATION

The National Power Survey projections of electric power generation, when translated into primary energy demand based on energy conversion efficiencies now demonstrated and anticipated during the next several years, indicate a continuing growth in fuel consumption in the form of coal, oil, and gas. Projected requirements of these fuels for electric power generation in terms of coal equivalent quantities is shown in Figure 5.

The most remarkable element of this projection is the very rapid decline in the rate of growth of natural gas usage for electric power generation. This projection is supported by a variety of gas curtailment cases currently before the Commission. It means, of course, that gas, the only "clean" fossil fuel, cannot be counted on to make a significant contribution to the reduction of undesirable emissions from electric power plants. The use in 1969 of the various fossil fuels for electric power generation expressed in their customary units of measure was 310 million tons of coal, 251 million bbls. of oil, and 3486 billion cubic feet of gas.

CURRENT QUALITY OF FUELS

Figure 6 prepared from information collected in FPC Form 67 shows the quantities of coal at the various sulfur levels consumed by electric utilities in 1969. The 303 million tons of coal burned by electric utilities reporting in 1969 ranged in sulfur content from 0.4 percent to as much as 6 percent by weight. The bulk of the coal, however, was in the two to four percent sulfur range; the weighted average was 2.58 percent. The distribution curve is bimodal, with one peak at below one percent sulfur. This, most likely, reflects an early response by several utilities to local air pollution control regulations requiring the use of fuels with less than one percent sulfur.

The quality of coal burned by electric utilities in 1969 was compared plant-by-plant and state-by-state with regulations in state implementation programs. About 44 million tons of coal consumed by electric utilities in 1969 in 255 units could meet the standards; whereas, 259 million tons with an average sulfur content of 2.81 percent was burned in 1010 units that could not meet standards and would require control measures.

Likewise, Figure 7 shows the quantities of oil at various sulfur levels consumed by electric utilities. Similarly, the sulfur content of the oil used in 1969 ranged from a fraction of a percent to nearly 3 percent, with a major portion of the oil in the 1.4 to 2.6 percent sulfur range. The weighted average was 1.66 percent. In the case of the oil distribution curve, three peaks were observed. One peak at 0.3 percent. Another at slightly below the one percent sulfur level, and the largest peak at an average sulfur content of 1.9 percent. Both peaks under 1 percent sulfur undoubtedly reflect response to local sulfur emission control regulations.

The quality of the oil burned by electric utilities in 1969, compared plant-by-plant and state-by-state, with the preliminary state implementation programs showing that 59 million bbls. of oil burned in about 310 units could meet the standards and that 199 million bbls. of oil burned in 735 units would require some type of control measures to meet the proposed sulfur limitations.

Table V shows fuel requirements projected in the National Power Survey. In 1975 when state plans are to be fully implemented, except where a two-year extension is asked, 425 million tons of coal will be required and 565 million bbls. of oil will be needed.

FOSSIL-FUEL REQUIREMENTS
FOR ELECTRIC POWER GENERATIONS

YEAR	COAL (Million Tons)	OIL (Million Bbls)	GAS (Billion Cu. Ft.)
1969	310	251	3486
1970	322	332	3894
1975	425	565	4110
1980	500	640	3800

Table V

Consider company plans for supplies of low sulfur fuels to get an order of magnitude of added supplies of low sulfur fuels that would be required in 1975 if control devices were not in operation at the electric generating units.

The National Coal Policy Conference estimated about a year ago that there would be 300 million tons of new mine capacity

by 1975 of which 75 million tons would be in low sulfur coal. Assume 2/3 or 50 million tons could be dedicated to the electric utilities. This quantity added to the 45 million tons of low sulfur coal which already meets the standards yields 94 million tons of naturally occuring low sulfur coal that could be available in 1975. Subtracting 94 million tons from the 425 million tons to total requirement leaves 331 million tons of high sulfur coal which will be burned in utilities with devices. Or in the absences of devices, this quantity of coal must be processed to low sulfur standards.

On the oil side, the Bureau of Mines in August 1970 in its study on Oil Availability by Sulfur Levels estimated the additional U.S. and Caribbean residual desulfurization capability would be around 300 million bbls. This added to the 59 million bbls. of low sulfur oil which already meets the standards yields a total of 359 million bbls. of low sulfur oil in 1975. Deducting this quantity from the total utility requirement of 565 million bbls. leaves about 206 million bbls. that will be burned in utilities with control devices, or in the absence of devices, 206 million bbls. must also be processed to low sulfur.

SUMMARY

The Clean Air Amendments of 1970 and the accompanying regulation have intensified the demand for "clean" fuels and control devices on a nationwide bases. These control measures must be in operation by 1975 or in some instances 1977.

In general there will be a demand for 425 million tons of low sulfur coal and 565 million bbls. of low sulfur oil. The majority of this will require some type of processing. Clean fuels are a preferred pollution control for electric generation because they are fail-safe and compatible with load changing characteristics of power plant operations. About 94 million tons of naturally occuring low sulfur coal and 359 million bbls. of low sulfur oil can be foreseen as a possible supply that meets air quality regulations. About 331 tons of coal and 206 bbls of oil will be burned in anywhere from 1300 to 1400 units each requiring control devices in operation in 1975. To the extent that control equipment manufacturers have a deficiency in these numbers of units operating in 1975, an equivalent demand will appear for processing portions of each of the high sulfur quantities of coal and oil.

The challenge is great, the time is short. Achievement of the ambient air quality objectives by the electric power industry in th'at short a period of time will require the utmost effort on the part of suppliers of low-sulfur fuels and manufacturers of sulfur emission control equipment, dedication on the part of the electric power industry, a great deal of investment capital, and the cooperative spirit of environmental groups and the public.
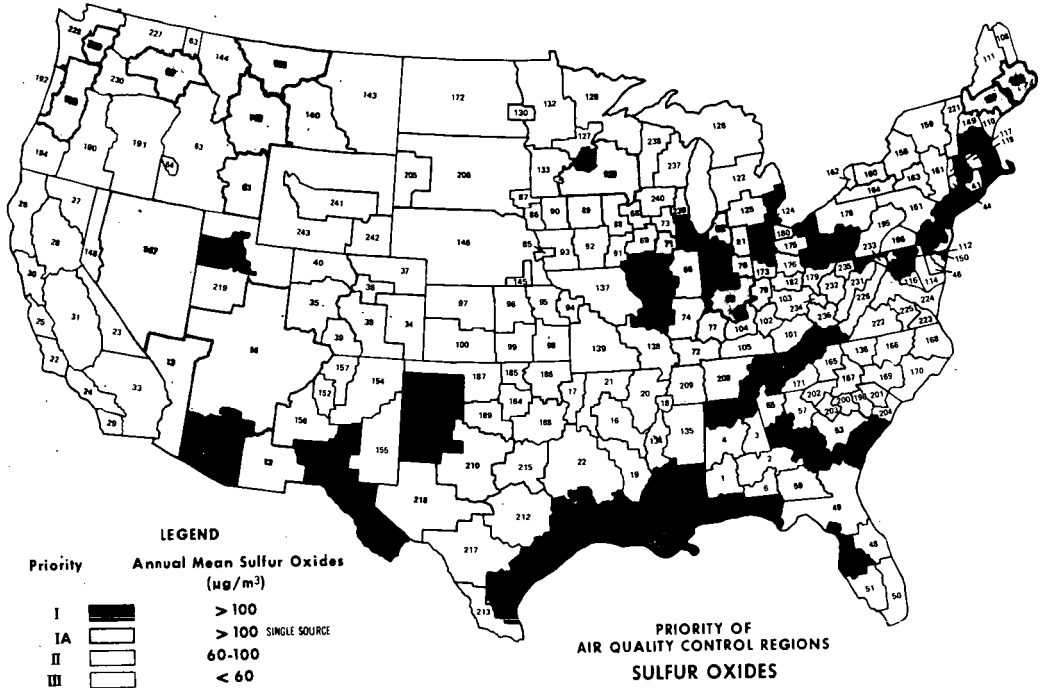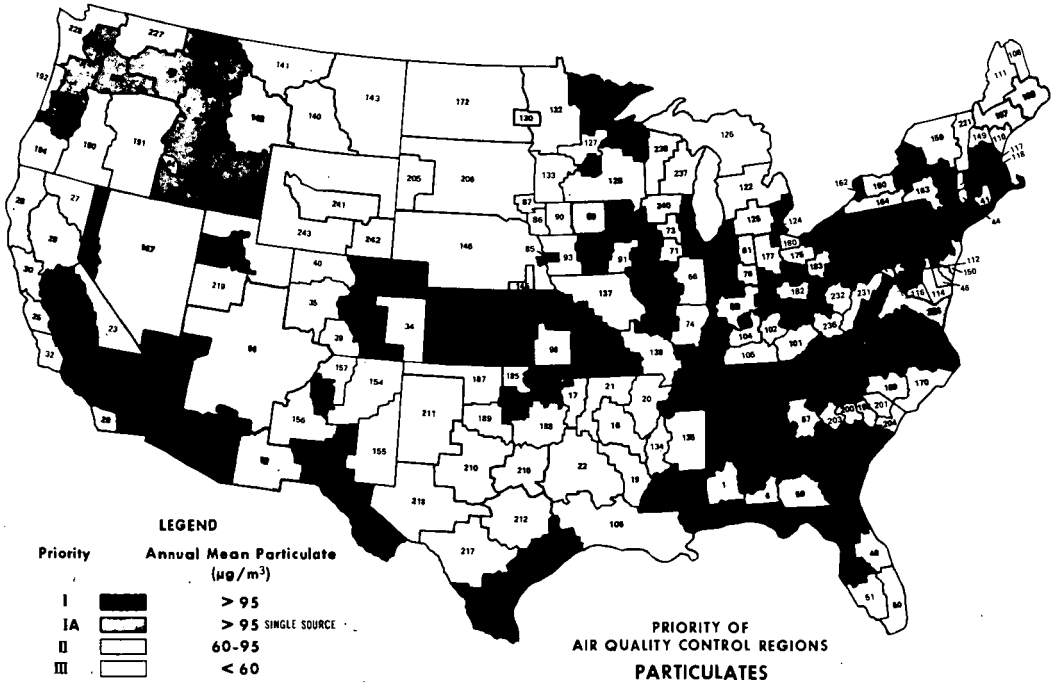
Figure 1

Figure 2

ESTIMATED ANNUAL ELECTRIC UTILITY GENERATION BY PRIMARY ENERGY SOURCES
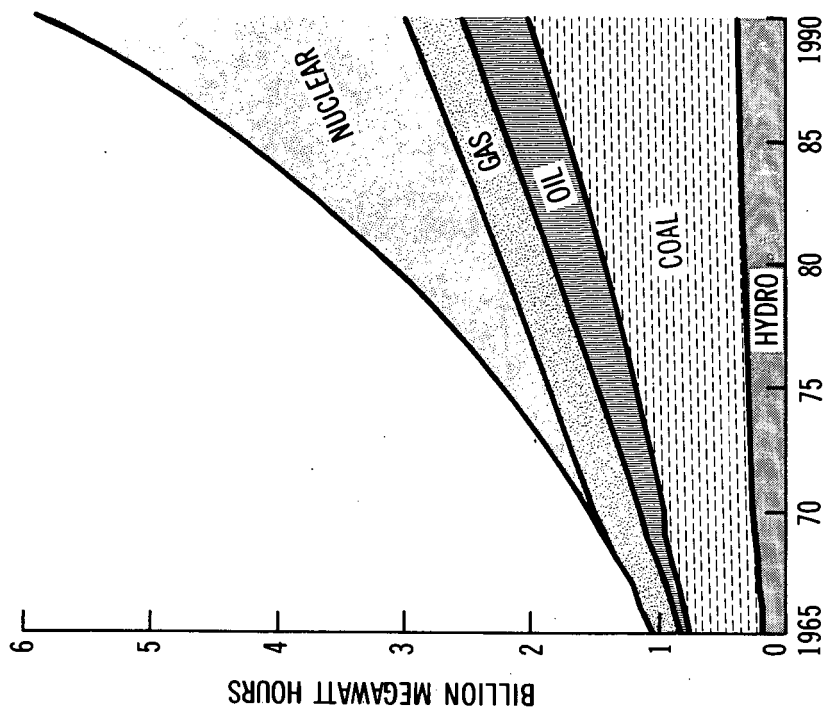
Figure 4

PROJECTED GENERATION MIX

Figure 3

DISTRIBUTION OF SULFUR CONTENT OF COAL BURNED BY ELECTRIC UTILITIES (1969)
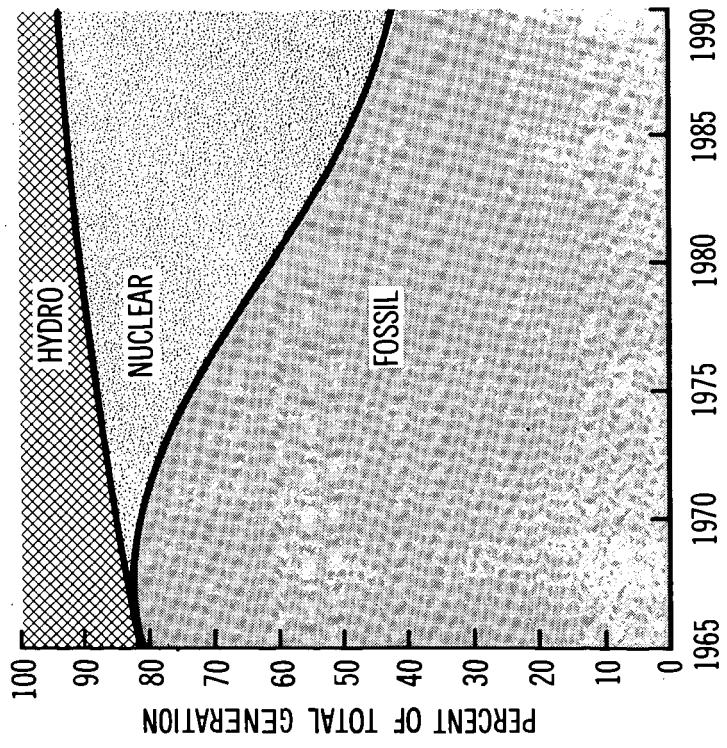
Figure 6

ESTIMATED ANNUAL FOSSIL FUEL REQUIREMENTS FOR ELECTRIC UTILITY GENERATION
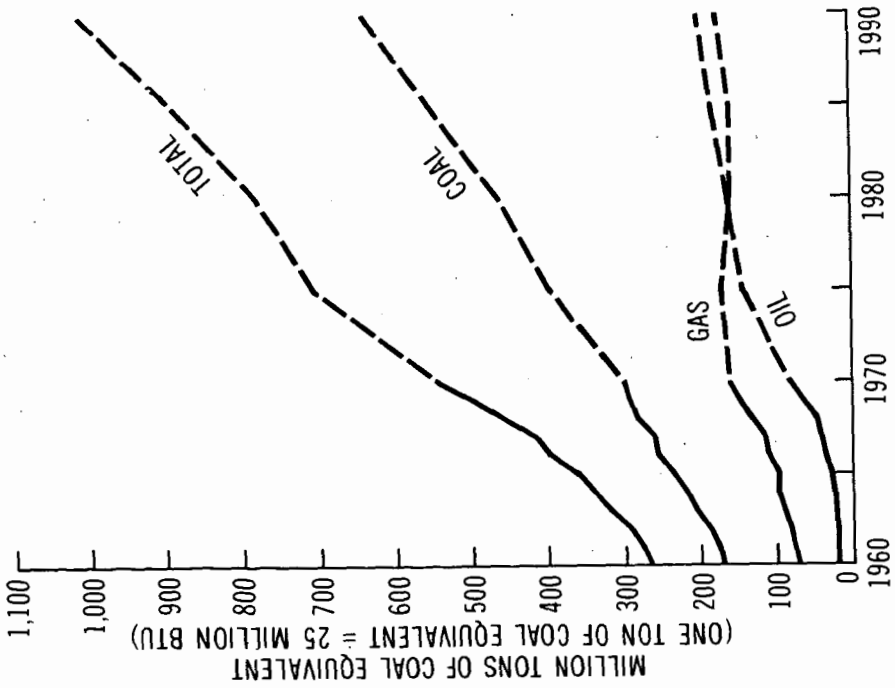
Figure 5

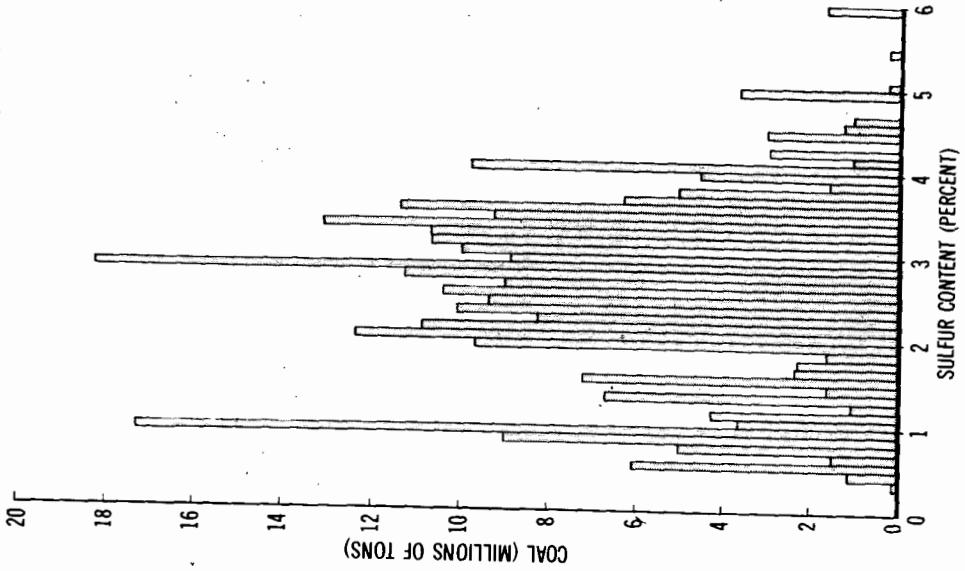## DISTRIBUTION OF SULFUR CONTENT OF OIL BURNED BY ELECTRIC UTILITIES (1969)
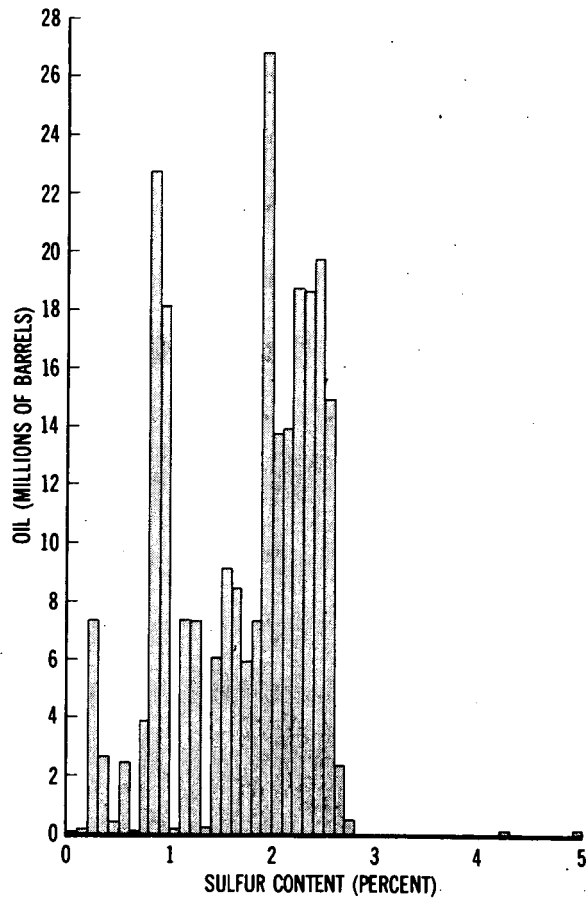

Figure 7

<u>The Effect of Desulfurization Methods on Ambient Air Quality</u> by <u>Kurt E. Yeager</u>,
Environmental Protection Agency, Washington, D.C. 20460

    The environmental constraints on the use of coal and oil will be described with
emphasis on sulfur oxide and particulate emissions and their relation to ambient air
quality. These relationships will be developed for three major fossil fuel fired
emitter categories; i.e. utility power plants, industrial combustion, and commercial/
residential combustion.

    Based on the relationships between emissions and ambient air quality, various
strategies for the achievement of ambient air quality standards will be developed.
These control strategies will consider the following alternatives for achieving the
required levels of emission control, both individually and in combination : (1) ef-
fluent treatment, (2) fuel treatment, and (3) fuel switching. The analyses will
consider the degree of air quality improvement, in terms of population achieving the
ambient air quality standards, relative to the cost and time necessary to implement
the control strategy.